

SCHOOL OF
CIVIL ENGINEERING

INDIANA

DEPARTMENT OF TRANSPORTATION

JOINT HIGHWAY RESEARCH PROJECT

FHWA/IN/JHRP-92/7

Final Report

CHEMICAL ADMIXTURES FOR HIGHWAY
CONCRETE: FUNDAMENTAL RESEARCH
AND A GUIDE TO USAGE

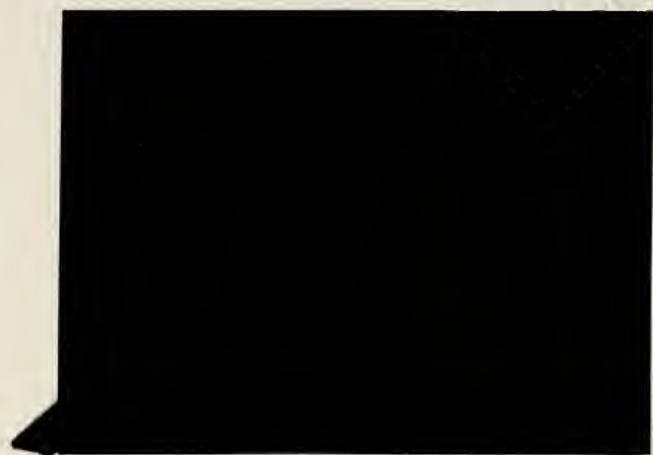
Sidney Diamond

Keisuke Matsukawa



PURDUE UNIVERSITY





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FUNDAMENTAL RESEARCH AND A GUIDE TO USAGE

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and the

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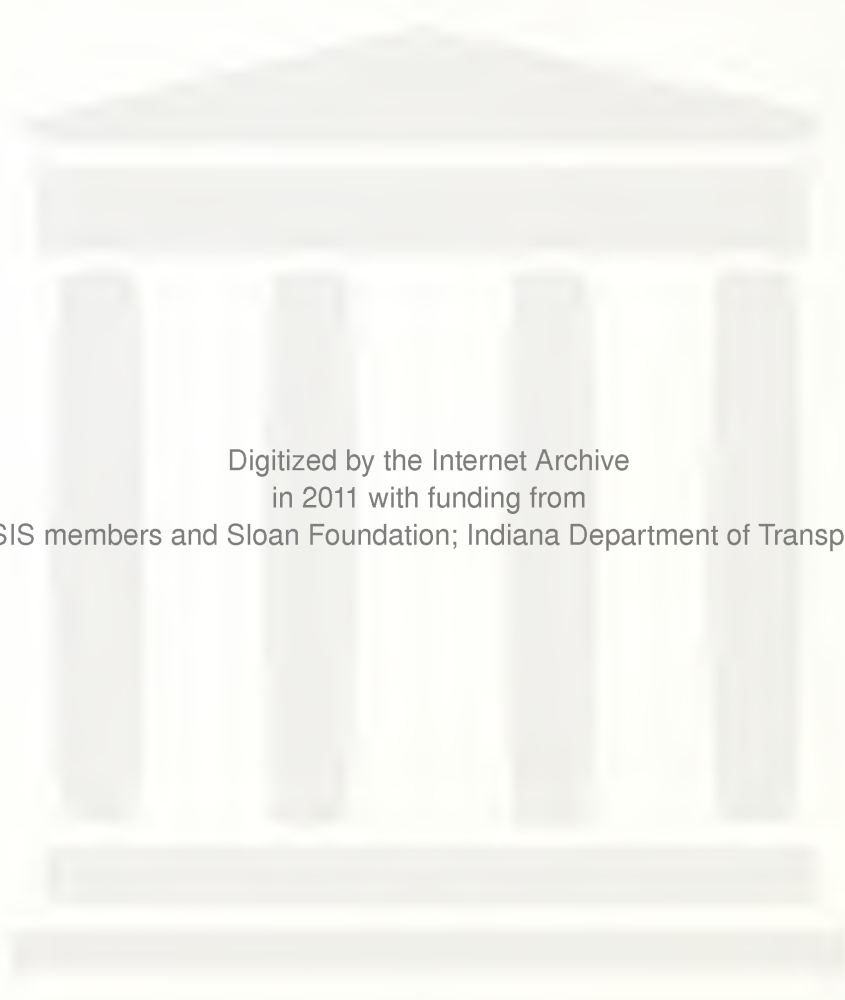
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16. Abstract This report is made up of two distinct elements. Part I is a guide to the current status and potential use of chemical admixtures for concrete, designed for the information and guidance of State DOT engineers. A historical prospective is given on chemical admixtures in concrete, and information is provided on the nature and practices of the concrete admixtures industry. Selection of and specifications for admixtures by State DOTs is reviewed, and a guide to the usage of specific classes of admixtures currently and potentially available is provided. Part II consists of a detailed record of laboratory research carried out to develop a pattern for physicochemical investigation of admixture effects. The procedures developed were then applied to the study of the detailed chemical interactions undergone by several different kinds of superplasticizer admixtures studied with a range of cements displaying various characteristics. Specific conclusions were drawn concerning the effects on superplasticizer effectiveness of certain cement characteristics, especially nature of the gypsum component and of cement alkali content.			
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We also thank Ward Malisch and the Aberdeen Group for permission to reproduce the comprehensive listing of chemical admixture marketers given in Part I Table 1.

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GENERAL INTRODUCTION

This project was originated with two distinct but related objectives in mind:

1. To review, evaluate, and interpret current practices with respect to the use of chemical admixtures in ordinary concrete. This effort might hopefully lead to a set of recommendations as to how current generation chemical admixtures coming into widespread use in other segments of the concrete based construction industry can best be applied for highway and other transportation-related concretes. The product of this portion of the study was visualized as being in the form of a guide to current types of admixtures and to benefits to be expected from their utilization. Information on comparative costs and cautions concerning proper use and possible problems might be included.
2. To carry out basic research in the area of how chemical admixtures function in concrete. Chemical admixtures are normally dissolved in the mix water. Their effectiveness to a considerable extent depends on maintaining a reasonable concentration level of these materials in the fluid phase of the concrete over the relevant period of activity. Very little information on concentration levels exists. Thus one objective was to develop methods for determining this and measuring changes in concentration over time. We then proposed to use this newly developed technology to study the behavior and interactions of one or more current generation admixtures used with a range of cements, including cements typically encountered in Indiana highway concretes.

This Final Report is thus a composite of two parts, designed separately to meet the two objectives. Separate introductions sections have been provided for each part.

Part I deals with the complicated overall situation with respect to the use of chemical admixtures in concrete, and contains sections on the history of chemical admixtures for concrete, on the unique features of the chemical admixture industry as presently constituted, and on typical practices in State Departments of Transportation with respect to specifications and control of the use of chemical admixtures. It then provides a profile of each of the major types of admixtures used in the various segments of the concrete construction industry, including chemical type, promised benefits, degree and area of current usage, and possible problems. Some idea of the potential for use of the specific admixture in various highway applications is provided.

One of the many complications that has overtaken this study during the course of its compilation is the very substantial growth of the use of certain mineral admixtures, including fly ash of several types, silica fume, and ground granulated blast furnace slag in concrete, both for highway and non-highway applications. The use of mineral admixtures strongly influences the conditions under which chemical admixtures function in concrete, in some cases the reverse is true as well. A section briefly describing these mineral admixtures and their influences on the behavior of chemical admixtures is included at the end of Part 1.

Part II reports the results of a complex and detailed series of laboratory investigations that formed part of the Ph.D. thesis investigation of Dr. Keisuke Matsukawa, carried out under the supervision of the writer. Dr. Matsukawa chose naphthalene sulfonate superplasticizer as his pilot chemical admixture. He developed a specific analysis for the content of this material in the fluid phase: i.e. the original mix water, and after set, the solution remaining in the pores of the hardened cement paste. He then developed the procedure for conducting repeated analyses at short intervals to determine how the concentration changes over time. At the same time he measured the effects produced

by the presence of the admixture on the concentrations of the cations and anions normally present in cement mix water. He also monitored the changing physical properties of the cement paste, and finally, the corresponding changes in gypsum, hemihydrate, and ettringite contents of the solid phase. All of these analyses, taken together, provide for the first time a complete and accurate picture of what the specific admixture at the specific dosage used was doing to the particular cement it was used with. This provides a pattern for laboratory investigations of admixture effects that had not previously been available.

The pattern was then applied to various dosage levels of two different naphthalene sulfonate superplasticizers on three different cements. Subsequently the pattern was applied to study the effects of malamine sulfonate superplasticizer .

The effectiveness of superplasticizers was found to be intimately associated with the concentration of sulfate ions being maintained in the mix water by the particular materials used. In order for a superplasticizer to maintain its dispersing action and not undergo slump loss, it must maintain a reasonable concentration in solution. Cement mixes that do not do so were found to stiffen and set prematurely. This response was found to be specifically associated with a low concentration of sulfate ions solution; adding sulfate reduces the early uptake of superplasticizer and allows the admixture to continue to function properly.

The superplasticizer level in solution was found generally to be quickly reduced by uptake into the early cement hydration products. The degree of this uptake was inversely correlated with the maintenance of superplasticizer effectiveness. Surprisingly, it was found that the early uptake of superplasticizer by some cements was, under some circumstances, spontaneously reversible after a few hours.

It was found that the pattern of ettringite development in early cement hydration, which strongly influences setting behavior, is much affected by the by the presence and concentration of the superplasticizer.

Most commercial naphthalene sulfonate superplasticizers are alkali neutralized. It was found that the use of such an admixture strongly affects the alkali and OH ion relationships that develop in the pore solution of the resulting concrete. The neutralizing alkali ions (normally Na^+) are immediately detected in the mix water. As the dissolved superplasticizer polymer chains are taken up by the hydrating cement, the sulfonate (SO_3H^-) charged sites on the chains are lost to the solution, but they are immediately replaced by an equivalent number of hydroxyl (OH^-) ions. The net effect is a permanent increase in the concentration of OH^- ions, and a corresponding greater potential for subsequent alkali aggregate reactions.

Studies were also carried out on the behavior of melamine sulfonate superplasticizers. These constitute a second family of superplasticizers that are not used as widely as naphthalene sulfonates superplasticizers, but still account for a significant proportion of total usage. They were found generally to behave in the same manner as naphthalene sulfonate-based admixtures.

While these studies did not specifically address the effects of mineral admixtures (i.e. fly ash, silica fume, etc.) on the behavior of the chemical admixtures studied, the basic knowledge developed provides a means of predicting what such joint effects might be. Thus it represents a permanent contribution to understanding the chemical fundamentals of what may take place when complex combinations of admixtures are used in concrete, for highway purposes or otherwise.

PART I

CHEMICAL ADMIXTURES IN HIGHWAY CONCRETE: BACKGROUND, HISTORY, AND FUTURE APPLICATIONS

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INTRODUCTION

The historical background to this compilation stems in part from, and relates directly to, the changing nature of State agencies responsible for highways and other transportation facilities. Historically, the present State Departments of Transportation are direct lineal descendants of state highway departments, which had as their prime and often sole charge the construction and maintenance of highway networks. A typical example is the present Indiana Department of Transportation (INDOT), which came into existence in 1989 as a direct descendent of the former Indiana Department of Highways (IDOH). There has been comparatively little new construction activity since highway departments changed over to DOTs, and practices, at least with respect to concrete, have probably not changed very much.

By far the largest volume of concrete placed under State Highway Department auspices was for highway pavements, with much smaller volumes being specified for appurtenant structures and specialized structures such as bridge decks. Separate specifications have been, and continue to be listed for bridge deck concrete and for "structural" concrete; such concrete necessarily is of higher standard than the specifications usually require for pavement concrete.

Historically, the only chemical admixtures normally specified for pavement concretes were air entraining agents, used to insure an adequate air-bubble system for freeze-thaw durability. Other admixtures often were permitted, especially for structural and bridge deck concrete. While these admixtures were specified on the basis of their meeting AASHTO (and indirectly, ASTM) standards, they have been selected and used primarily on the representations of admixture suppliers and the experience of local contractors.

The actual extent of use of admixtures on highway jobs has always been much less than on building construction and other concrete applications. Consequently, State Highway Department engineers, even concrete specialists in the central state highway laboratories and offices of the Engineer of Materials, seem to have had only limited opportunities to become familiar with them. A further factor was (and is) the relative uneasiness of most civil engineers in dealing with complex chemical matters. Thus

when present trends began to develop involving the development of many new chemical admixtures, widespread use of these in conjunction with fly ash and in some cases silica fume, and highly successful applications of both to building construction and other non-highway applications, the need for additional guidance specifically directed toward State DOT engineers became manifest. This portion of the final report represents an attempt to at least partially meet this need.

To some extent the time scale under which this work was undertaken, and delays due to the writer's medical difficulties, have reduced the need for this report. Other agencies have been active in the intervening period in promoting and providing guidance on admixture use. For example, the Federal Highway Administration has in the past few years conducted a series of demonstration project meetings under the designation "Effective Utilization of Portland Cement Admixtures", to acquaint State DOT engineers with the fundamentals of chemical admixtures in concrete. Transportation Research Board Committee A2-E05 has recently published a 50-page guide on "Admixtures and Ground Slag for Concrete" (Transportation Research Circular 365, Dec. 1990). The American Concrete Institute has maintained an active program of seminars in various locations entitled "How to Effectively Use the Newest Admixtures", and a Seminar Course Manual (SCM-23 (90)) is available. Nevertheless, the writer feels that this compilation still can fill an important need.

HISTORICAL PERSPECTIVE ON CHEMICAL ADMIXTURES

For many years concrete "recipes" contained only Portland cement, coarse and aggregate, sand, and water. The use of other prospective components, including chemical admixtures, were actively discouraged by well respected and influential agencies on the grounds that they were simply not needed and could be detrimental.

After the accidental discovery that air-entraining agents might be successfully used in concrete to prevent freeze-thaw damage, and the widespread adoption of this first chemical admixture, the way was opened for the development and marketing of a great variety of chemical materials to use in concrete mixes for a variety of perceived purposes. Companies specializing in this area were founded, and a recognized chemical admixture industry came into being. In the United States, after a period of development, ASTM codified these chemical admixtures into several classes, based on their intended effects. Set accelerators, set retarders, water reducers, and combination pur-

pose admixtures were recognized and standardized tests were adopted to measure and hopefully predict their effectiveness. AASHTO subsequently adopted essentially the same system for the special needs of highway and transportation agencies.

More recently, the class of "official" chemical admixtures has been broadened to include superplasticizers ("high-range water reducers") and combined superplasticizer-retarders.

However, the "official" admixtures have been in recent years augmented by a rapidly growing collection of chemical admixtures designed for new purposes. Prominent examples include admixtures to help prevent corrosion of steel in concrete, "stop-start" admixture packages that permit a suspension of the hardening of fresh concrete and its resumption after as much as several days, antifreeze admixtures, admixtures to reduce the cracking induced by excessive shrinkage by lowering the surface tension, and others. These are in addition to specialized admixtures designed for use by cement manufacturers (i.e. grinding aids) and admixtures for specialized forms of concrete construction such as shotcrete, pumping aids, etc.

The picture has become even more complex with the much more widespread use of mineral admixtures such as silica fume, fly ash, and ground granulated blast furnace slag. Silica fume acts in concert with superplasticizers to substantially reduce the water demand in concrete, to a far greater extent than can be accomplished by superplasticizers alone; however, by itself, silica fume generally increases water demand. In consequence, high performance concrete based on silica fume incorporation necessarily requires accompanying use of superplasticizer (or sometimes very heavy doses of water reducers). Some fly ashes have similar characteristics, and high performance concretes based on fly ashes usually also require heavy doses of one or the other of these chemical admixtures. However, fly ashes and slags are also widely used in more conventional concrete, including concrete for highway purposes. Indeed , chemical admixture manufacturers are currently marketing "new generation" admixtures, such as air entraining agents, said to be designed to work specifically with concrete containing mineral admixtures.

Because of this proliferation, the present state of affairs with regard to chemical admixture selection and use in concrete may be even more confusing than it has been previously. Certainly combinations of chemical admixtures are more frequently prescribed, and combinations of chemical and mineral admixtures are becoming recognized tools in the design of practical concretes. The potential for problems, particularly for problems reflecting negative interactions, is thus multiplied. On the other hand, the new tools have provided so much improvement in concrete properties and in potential

durability that their judicious use cannot be avoided if the responsible engineer is to properly fulfill his function in producing the best and most durable transportation structures at the least cost.

THE CONCRETE ADMIXTURES INDUSTRY

To understand how and what admixtures should be used in a given situation, it is helpful to understand how concrete admixtures are produced and marketed. Such information is not usually available in published form, and because of this some State DOT engineers tend to be a little bewildered by some of the seemingly arcane practices associated with the concrete admixtures industry.

Concrete admixture marketing began in the United States. The first products marketed to concrete producers were air entraining agents, based on a waste product derived from tree stumps ("vinsol" resin, short for "very insoluble" resin - material left over after various more soluble components had been extracted for other uses). Waste products of various kinds have been widely used in chemical admixture industry formulations since then.

However, in more recent years, admixture manufacturers have typically moved beyond by-product compounding, and have employed extensive technical staffs and conducted highly sophisticated chemical and manufacturing research to formulate and efficiently produce their newer products.

The chemical admixtures industry in the United States has grown from a few producers to a relatively large number of firms. The journal "Concrete Construction" annually publishes a classified list of suppliers of various materials to the concrete construction industry. In the December 1991 issue, the lists include 38 suppliers of accelerating admixtures, 30 suppliers of air-entraining agents, 26 suppliers of retarding admixtures, 29 suppliers of water reducing admixtures, 33 suppliers of superplasticizers, and 17 suppliers of corrosion inhibiting admixtures. The separate lists, of course, contain many duplications, and "only" 65 separate firms are included. The combined listing of all of these firms is provided as Table 1, through the kind permission of Concrete Construction .

These firms encompass a wide variety of sizes and characteristics. The industry has historically consisted of a small group of companies marketing nationally, and a rather larger group of companies marketing regionally, often with limited product lines, but sometimes with great success due to their ability to service local markets. While market share figures are not ordinarily released, it is generally understood that

Table 1.

Marketers of Chemical Admixtures as of Jan. 1, 1992

(Listing Provided through the Courtesy of the Aberdeen Group,
Publishers of Concrete Construction)

1. Air-Entraining Agents

Anti Hydro
 Arcal Chemicals
 AXIM Concrete Technologies
 Carroll
 Conchem
 Concrete Producers Dept Store
 Cormix Construction Chemicals
 DFC
 Durafiber Group/
 Hill Brothers Chemical
 Elastizell
 Euclid Chemical
 Fosroc
 Fox Industries
 Fritz Chemical
 Gibco
 W R Grace
 Handy Chemicals
 I A I
 M & L Testing Equipment
 Master Builders
 W R Meadows
 Monex Resources
 Nox-Crete
 PQ
 Select Products
 Sika
 Specco Industries
 Sternson Group
 Texmastic International
 Universal Fastening
 & Concrete Accessories

2. Accelerators

Anti Hydro
 Aqua-Flo
 Arcal Chemicals
 AXIM Concrete Technologies
 Berylex National Sales
 Carroll
 Cemtech Laboratories
 Chargar
 Conchem
 Concrete Producers Dept Store
 Conproco
 Conspec Marketing & Mfg.
 Cormix Construction Chemicals
 Dow Chemical U S A

Durafiber Group/
 Hill Brothers Chemical
 Dur-O-Wal
 Euclid Chemical
 Fosroc
 Fox Industries
 Gemite Products
 W R Grace
 Handy Chemicals
 A C Horn
 I A I
 Lafarge Calcium Aluminates
 Lambert
 Master Builders
 W R Meadows
 Monex Resources
 National Varnish
 Nordic's-Viking Concrete Products
 Quikrete Companies
 Sika
 Southern Grouts & Mortars
 Specco Industries
 Spray-Crete Industries
 Texmastic International
 Universal Fastening &
 Concrete Accessories

3. Retarders

Anti Hydro
 Arcal Chemicals
 AXIM Concrete Technologies
 Boremco Specialty Chemicals
 Conchem
 Concrete Producers Dept Store
 Cormix Construction Chemicals
 Durafiber Group/
 Hill Brothers Chemical
 Euclid Chemical
 Fosroc
 Fox Industries
 Fritz Chemical
 Geistlich International
 W R Grace
 Haarmann & Reimer
 I A I
 Master Builders
 Monex Resources
 Old North Mfg
 Onoda
 L M Scofield
 Sika

Specco Industries
 Specrete-IP
 Texmastic International
 Universal Fastening &
 Concrete Accessories

4. Water Reducers

Anti Hydro
 Arcal Chemicals
 AXIM Concrete Technologies
 Berylex National Sales
 Boremco Specialty Chemicals
 Conchem
 Concrete Producers Dept Store
 Cormix Construction Chemicals
 Durafiber Group/
 Hill Brothers Chemical
 Euclid Chemical
 Fosroc
 Fox Industries
 Fritz Chemical
 Geistlich International
 Gibco
 W R Grace
 Haarmann & Reimer
 Handy Chemicals
 I A I
 Lambert
 Master Builders
 Monex Resources
 Nox-Crete
 L M Scofield
 Sika
 Specco Industries
 Specrete-IP
 Texmastic International
 Universal Fastening &
 Concrete Accessories

5. High Range Water Reducers (Superplasticizers)

Anti Hydro
 Arcal Chemicals
 AXIM Concrete Technologies
 Boremco Specialty Chemicals
 Conchem
 Concrete Accessories
 Concrete Producers Dept Store
 Cormix Construction Chemicals
 Durafiber Group/
 Hill Brothers Chemical
 Euclid Chemical
 Fibrin
 Fosroc
 Fox Industries
 Fritz Chemical
 Gemite Products
 Geochemical

Gibco
 W R Grace
 Handy Chemicals
 I A I
 Lobeco Products
 Master Builders
 Metalcrete Mfg
 Monex Resources
 Norcem Concrete Products
 Nordic's-Viking Concrete Products
 Nox-Crete
 Onoda
 Sika
 Specco Industries
 Spray-Crete Industries
 Texmastic International
 Universal Fastening &
 Concrete Accessories

6. Corrosion Inhibitors

Atlas Minerals & Chemicals
 Concrete Producers Dept Store
 Elkem Materials
 Fosroc
 Fox Industries
 Gemite Products
 W R Grace
 IPA Systems
 Master Builders
 Monex Resources
 Norcem Concrete Products
 Nordic's-Viking Concrete Products
 Nox-Crete
 Onoda
 Sika
 Specco Industries
 Universal Fastening
 & Concrete Accessories

significant portion of the market is dominated by the two largest producers, W. R. Grace and Master Builders, Inc. Informed estimates suggest that their combined share of the total chemical admixture market in the United States may be in excess of 70 %. Other large producers include Cormix (incorporating admixtures formerly marketed by the Gifford Hill Co.), Euclid Chemical, Fosroc, Monex Resources, and Sika.

The large firms (and some that are not so large) are often owned by international conglomerates, many foreign owned. They have access to current technology drawn from many chemical and physical fields, and maintain extensive and well-equipped laboratories. Chemical admixture industries are very active in European countries and in Japan. While the industry was started in the United States, like many others, leadership may have passed to overseas competitors. The European industry, in particular is well organized and there is an active European Federation of Concrete Admixtures Associations (EFCA) headquartered in Frankfurt.

In the United States, recent experience indicates that the stability of various companies fluctuates drastically. Buy-outs, reorganizations, and sales of product lines are common. The industry is hotly competitive; new developments formulated by one firm are often quickly matched by competitors. Patent positions play an important role; the larger companies have extensive legal staffs and file many patent applications.

Despite this emphasis on modern technology and international development, marketing strategies seem not to have changed very much. From the beginning, technical service and problem solving have been most important components of the marketing effort, to a much greater extent than in other fields. Admixture suppliers have traditionally supplied a "full service" package to their customers, and have included the costs of such services in the price of the admixture. These services often include provision for providing and maintaining admixture dispensers, monitoring large jobs, and investigating causes of field problems.

This tradition generally continues, although some firms now market admixtures on a commodity basis, without the service, but at lower prices. Indeed, there are some indications that a few ready mix concrete producers are blending at least some of their own concrete admixtures from industrial raw materials.

Specific admixtures are often marketed under a general product line designation, and differentiated from each other by supplementary letter or numbers.

The usual practice in the industry is to guarantee that any product delivered will conformance with ASTM (or AASHTO) specifications, but not to guarantee that the specific product will always be formulated from the same components, nor indeed to identify the components beyond certain vague class designations. This industry prac-

tice is unlike that in most European countries, where admixture manufacturers typically are required to disclose the actual chemical ingredients used in their products. Thus in the United States the actual composition of a given admixture may change without the name of the admixture being changed. Indeed, different formulations may appear under the same product name in different regions. Conversely, the same product may carry different names in different markets.

Certain firms produce a specially-designated line of admixtures for the highway pavement market, which may or may not include the same materials produced for sale to the general concrete industry. Typically such admixtures are provided only in bulk, rather than in pre-packaged containers. A product sheet describing one such admixture ("Masterpave") is provided as an illustration in Figure 1. This and other product sheets reproduced in this report are for illustrative purposes only; no endorsement of any of the specific products or of the claims listed is expressed or implied.

Admixture companies characteristically produce a product sheet for each of their admixtures. These typically contain (1) a description of the product (2) the advantages claimed, (3) applicable ASTM or other standards that are claimed to be met (4) recommended dosage rates, (5) technical data (6) information on compatibility with other products (7) precautions that should be observed. Manufacturers generally advise close conformance to the suggested dosage rates and to the listed precautions. Manufacturers providing service to clients will generally, but not always so indicate by some statement like "For further assistance, consult your local X Company representative."

The product sheet that was shown in Figure 1 to illustrate a special product aimed at transportation departments is rather less specific than most product sheets aimed at the general market. Most product sheets are rather more detailed in the information provided. Product sheets from various manufacturers are included as illustrations in the various sections describing specific types of admixtures. Again, no endorsement of these specific products is implied.

One particular component of some admixtures deserves special mention. It has been well established for many years that the presence of chlorides in concrete promotes corrosion of embedded steel, and efforts have been made by many in the concrete field to eliminate all possible sources of chloride in reinforced and prestressed concretes. In accord with this trend, the current version of the ASTM standard specification for chemical admixtures for concrete (C 94 - 90) carries the proviso (Section 5.4) that "At the request of the purchaser, when the admixture is to be used in prestressed

MASTER BUILDERS**MASTERPAVE™***Admixture Products Information***DESCRIPTION:**

MASTERPAVE is a ready-to-use, liquid admixture expressly recommended for pavement concrete. It meets ASTM C 494 requirements, specifically:

- Increased Strength—compressive and flexural

- Relative Durability to Damage from Freezing and Thawing—well above industry standards
- Reduced Water Content Required for a Given Workability
- Normal-Setting Characteristics

ADVANTAGES:

MASTERPAVE admixture aids in the production of concrete which has the following special qualities in the plastic or hardened state:

Plastic Concrete

- Improved Texturing Characteristics
- Greater Edge Stability and Slump Control

- Improved Workability using less water
- Reduced Segregation
- Increased Placing Rate

Hardened Concrete

- Increased Compressive and Flexural Strengths
- Higher Early Strength

WHERE TO USE:

This admixture can be used in all paving-related concrete requiring normal set in combination with all the benefits of an effective, water-reducing admixture. MASTERPAVE admixture is chloride-free (less than 10 ppm by weight of cement).

MASTERPAVE admixture can be used with all air-entraining admixtures

approved under AASHTO, CRD and ASTM specifications, including Master Builders air-entraining admixtures.

When used in conjunction with another admixture, each admixture must be dispensed separately into the mix.

QUANTITY TO USE:

MASTERPAVE admixture is recommended for use at a rate of 4 to 6 fl oz per 100 lb (260 to 390 ml per 100 kg) of cement for most concrete mixes using average concrete ingredients. Because of variations in job condi-

tions and concrete materials, dosage rates other than the recommended amounts may be required. In such cases, contact your local Master Builders representative.



Figure 1. Product sheet describing an admixture marketed specifically for highway applications.

PACKAGING:

MASTERPAVE admixture is supplied in bulk.

**TEMPERATURE
PRECAUTION:**

Care should be taken to prevent MASTERPAVE from freezing. If it freezes, thaw at 35°F (2°C) or above

and completely reconstitute by mild mechanical agitation. **Do not use pressurized air for agitation.**

For additional information on MASTERPAVE admixture or on its use in developing a concrete mix

with special performance characteristics, contact your local Master Builders representative.

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CLEVELAND, OHIO 44122

concrete, the manufacturer shall state in writing the chloride content of the admixture and whether or not chloride has been added during its manufacture".

While comparatively little prestressed concrete is used for transportation purposes, highway bridge decks are heavily reinforced, and in most of the country are heavily subject to steel corrosion damage. Under the circumstances, the restriction of this provision to prestressed, rather than to both prestressed and reinforced concrete, seems curious. Some state DOTs have instituted more stringent requirements as part of their standard specifications. For example, the Indiana Department of Transportation specification carries provisions to the effect that no chloride can be deliberately added to an admixture in its formulation, and the total percentage of "incidental" chloride must be specified by the manufacturer.

SELECTION AND SPECIFICATION OF ADMIXTURES BY STATE DOTs

In the United States chemical admixtures for concrete generally are supplied as conforming to one or another of the relevant ASTM standards: ASTM C 260 - 86, Standard Specification for Air-Entraining Admixtures for Concrete; ASTM C 494 - 90, Specification for Chemical Admixtures for Concrete, and ASTM C 1017 - 90, Standard Specification for Chemical Admixtures for Use in Flowing Concrete. For highway and transportation use, the American Association of State Highway and Transportation Officials has adopted the substance of two of these specifications as M-154 (for ASTM C - 260), and M - 194 (for ASTM C-494). The specification for admixtures for flowing concrete has so far not been adopted by AASHTO.

In addition to the standard specifications referenced above, most State DOTs add specific requirements and exceptions based on local experience or practice. The volume of highway and transportation business has been historically great enough that suppliers will ordinarily meet such local amendments.

The usual practice is for prospective admixture suppliers to submit samples and results of testing directly to the relevant division of the State DOT. If the results are satisfactory the supplier is placed on the "Approved List" of suppliers for that particular class of material.

Some chemical admixtures, particularly the newer ones, are not covered by ASTM or AASHTO specifications. In some cases at least, appropriate specifications are under development, but the process is slow and because of commercial considerations the necessary consensus may be difficult to reach.

A GUIDE TO SPECIFIC CLASSES OF CHEMICAL ADMIXTURES

Air Entraining Agents

As has been previously mentioned, air-entraining agents were the original chemical admixtures, and are probably still the most widely used of the various types. Their widespread use is based not only on their ability to prevent freezing and thawing damage, but also on the desirable "buttery" character induced into the consistency of the fresh concrete. Other perceived benefits include lower permeable and absorptivity of the hardened concrete, and in some cases possibly increased resistance to the effects of sulfate attack and of alkali aggregate attack.

ASTM C 260 (and its AASHTO M-154 equivalent) specify certain performance characteristics not related to the primary function of the admixture, namely (a): a limitation on bleeding compared to the bleeding of the same concrete without the admixture; (b) a limitation on changes in setting time (no more than 1-1/4 hour retardation or acceleration); (c) limitations on both compressive strength and flexural strength reductions at any age of test (to no more than 10% of the reference strength without the admixture), with the flexural strength limitation being optional, and (d) a limitation on length change, to be no greater than 120% of that of the reference concrete after 14 days of drying. Strangely, the dosage of the admixture for these tests not prescribed, and is presumably the manufacturer's normal recommended dose rate.

The primary functional requirement specified for air entraining agents is that resistance to freezing and thawing measured by Procedure A of ASTM Test Method C-666 be established at a relative durability factor of 80%. Again, the dosage of air entraining agent to use to establish such effectiveness is not specified.

In point of fact, the effectiveness of a given air entraining agent in preventing freeze-thaw damage is well understood to be a function of the stability of the entrained air void system under the necessary field handling conditions, and in the last analysis, to the success of the agent in achieving a bubble spacing factor of the order of 0.01 in. or less. The freeze-thaw resistance of concrete is usually linked to the total air volume percentage, which may be specified differently for different classes of concrete and different conditions of exposure. However, the air entraining agent specifications neither

require nor permit the option of determining the effectiveness of a given air entraining agent in producing a given level of air entrainment or a given bubble spacing factor at any particular dosage rate.

Air entraining agents are ordinarily adsorbed at air-water interfaces, and reduce the surface tension of the water significantly. Some air entraining agents (those with insoluble calcium salts) precipitate solid or gelatinous films around entrained air bubbles. The sand content and gradation influence the amount of air entrained, especially in lean mixes, and such factors as cement content, consistency of fresh concrete, mixing effectiveness, temperature, and vibration may affect the air bubble system produced by a given air entraining agent.

Air entraining agents have been formulated from various classes of compounds. The classic "vinsol resin" products are primarily impure abietic and pimeric acids derived from pine stumps or from tall oil processing and neutralized, commonly with sodium hydroxide. Alkyl aryl sulfonates (which are classic detergents) alkyl sulfates, and phenol ethoxylates are among the other classes of compounds that have been used.

One of the particular characteristics that set air entraining agents apart from most admixtures is the extremely low dosage of active ingredient actually used. Air entraining agents are usually supplied as liquids which lend themselves to accurate batching by automatic dispensing equipment, but the actual content of surfactant batched is normally very low; values substantially less than 0.1% by weight of cement have been quoted. The small materials cost is usually offset by the greater yield (air being substantially less expensive than the volume of concrete it displaces), and by other savings sometimes attained in redesigning the concrete mix - for example reducing the sand content. The resulting very low net cost of the air entrainment is one factor responsible for its widespread use.

The dosage requirements in field applications, while small, may be influenced by mineral admixtures, especially silica fume and fly ash. The carbon content of the fly ash is of particular importance, since some of the admixture may be quickly adsorbed by the carbon and its air entraining effect lost. The influence of silica fume is less straightforward, but there have been suggestions that some traditionally effective air entraining agents do not produce as satisfactory an air bubble system when used with concrete containing silica fume. Partly in response to such concerns, some manufacturers have recently marketed "new generation" air entraining agents said to be specially effective with concretes incorporating silica fume and fly ash.

According to the current listing of producers of various types of concrete admixtures published in the December 1991 issue of Concrete Construction, 30 different firms

currently market air entraining admixture in the United States. the actual variety of products sold is substantially larger than this, some firms marketing a number of different air entraining agents.

A representative product sheet for one of the newer air-entraining agents is provided for illustrative purposes as Figure 2.

Accelerators

Accelerators are a class of chemical admixtures used primarily to facilitate cold weather concrete placement. A subsidiary use of these materials is to overcome a tendency to slow set; for this purpose they may be an element in a carefully compounded "prescription" admixture which otherwise would cause excessive retardation.

There is considerable confusion in the field as to whether accelerators are primarily supposed to accelerate concrete setting, or to accelerate the rate of strength gain after setting. ASTM C 494 -90, Standard Specification for Chemical Admixtures for Concrete, defines a Type C (accelerating) admixture as one that does both, but the two uses are not necessarily equally addressed by a given kind of accelerating admixture. The performance requirement of that specification for Type C admixtures requires that the time of initial set be advanced at least 1 hour, but not more than 3-1/2 hours, from that of the reference concrete, and the time of final set be advanced at least 1 hour. With respect to early strength gain, the requirement is that the 3-day compressive and flexural strengths be increased at least 25% and 10%, respectively, over that of the reference concrete. The specification also requires that there be no loss in compressive strength at 7 or 28 days, and that compressive strengths at 6 months and 1 year be at least 90% of those of the reference concrete. With respect to flexural strengths, the permitted effect over time is somewhat different; the specification is that there be no loss in flexural strength compared to the reference concrete at 7 days, and that the flexural strength at 28 days be at least 90% of that of the reference concrete. There are subsidiary requirements on shrinkage, and on freeze-thaw durability for air-entrained, concrete used with an accelerating admixture.

Historically the premier accelerating admixture has been calcium chloride, which is still the most effective accelerator available, and is extremely inexpensive to boot. Accelerators based on calcium chloride are available in liquid (solution) or in solid form, and are extensively marketed. However, as indicated earlier, the association of chloride at moderate concentration with corrosion of steel in concrete has rendered calcium

MASTER BUILDERS

MICRO-AIR*

Admixture Products Information

Admixture for Entraining Air in Concrete

DESCRIPTION:

MICRO-AIR is an air-entraining admixture which gives concrete extra protection by creating ultra-stable air bubbles that are strong, small and closely spaced—a characteristic especially useful in the types of concrete known for their difficulty to entrain and

maintain the air content desired.

Even when used at a lower dosage rate than standard air-entraining admixtures, MICRO-AIR meets the requirements of ASTM C 260, AASHTO M 154, CRD-C 13 and other Federal and State specifications.

ADVANTAGES OF AIR ENTRAINMENT:

The entrainment of optimum air content in concrete results in the following improvements in concrete quality:

- Increased resistance to damage from freeze/thaw cycles and to scaling from deicing salts

- Reduced permeability—increased watertightness
- Reduced segregation and bleeding
- Improved plasticity and workability

ADVANTAGES OF MICRO-AIR:

- Greatly improved stability of air entrainment
- Improved air-void system in hardened concrete
- Improved ability to entrain and retain air in low-slump concrete; concrete

containing high-carbon-content fly ash; concrete containing large amounts of fine materials; concrete using high-alkali cements; high-temperature concrete; and concrete with extended mixing times.

FEATURES/BENEFITS:

Ready to Use—Solution is the proper strength for accurate dispensing.

Compatible for Use—MICRO-AIR admixture is compatible with concrete containing other admixtures or admixture systems—water-reducers, high-range water-reducers, accelerators, retarders, densifiers and water repellents. It also increases the entrained air content of concrete made with air-entraining portland cement.

The use of MICRO-AIR air-entraining admixture with Master Builders Pozzolith[®] admixtures forms a desirable combination for producing the highest quality, normal or lightweight concrete. Heavy-weight concrete normally does not contain entrained air.

NOTE: As stated in ACI 212 and other publications, when two or more admixtures are used, they must be added to the mix separately (through dispensers or manually) and must not be mixed with each other prior to adding to the concrete mix.

For optimum, consistent performance, the air-entraining admixture should be dispensed on damp, normal or heavy-weight fine aggregate. When using lightweight fine aggregate, field evaluations should be conducted to determine the best location to dispense the air-entraining admixture—on the damp fine aggregate or with the initial batch water.

¹Concrete durability research has established that the best protection for concrete from the adverse effects of freeze/thaw cycles and deicing salts results from: • proper air content in the hardened concrete; • a suitable air-void system in terms of bubble size and spacing; and • adequate concrete strength, assuming the use of sound aggregates and proper mixing, placing, handling and curing techniques.

Control of air content should be based upon determinations made on concrete at the time of placement, following adjustment of the batch to proper consistency (slump). The rate of use of an air-entraining admixture depends on the air content to be obtained along with many other factors. The amount normally required is reduced by the introduction of a water-reducing, set-controlling admixture.

When unusually low amounts of an air-entraining admixture are sufficient to achieve normal ranges of air content or if the required amount of air-entraining admixture necessary to achieve required levels of air content is observed to decrease significantly under given conditions, the reason for this change should be investigated. In such cases, it is especially important to determine: (a) that a proper amount of air is contained in the fresh concrete at the point of placement; and (b) that a suitable air-void system (spacing factor) is being obtained in the hardened concrete.

*Reg. U.S. Pat. & Tm. Off.



Figure 2. Product sheet describing one of the newer air-entraining agents.

USAGE INFORMATION:

1. MICRO-AIR admixture is a ready-to-use solution. Do not mix it with any other admixture.
2. Add MICRO-AIR admixture to the concrete mix using a dispenser designed for air-entraining admixtures; or add manually using a suitable measuring device that ensures accuracy within plus or minus 3% of the required amount.
3. There is no standard dosage rate for MICRO-AIR admixture. The exact quantity of air-entraining admixture needed for a given air content of concrete is not predictable because of differences in concrete-making materials. Typical factors which might influence the amount of air entrained are: temperature, cement, sand grading, sand-aggregate ratio, slump, means of conveying and placement, use of extra fine materials such as fly ash, etc.
The amount of MICRO-AIR admixture used will depend upon the amount of entrained air required under actual job conditions. In a trial mix, use 1/8 to 1-1/2 fl oz/100 lb (8 to 98 ml/100 kg) of cement. In mixes containing water-reducing, set-controlling admixtures, the amount of MICRO-AIR needed is somewhat less than the amount required in plain concrete. In mixes requiring a significantly higher or lower dosage to obtain the desired air content, consult your local Master Builders representative.
4. Measure the air content of the trial mix and either increase or decrease the quantity of MICRO-AIR admixture to obtain the desired air content in the production mix. Check the air content of the first batch and make further adjustments if needed. Frequent checks during the course of the work should be made since factors mentioned in paragraph 3 above may require adjustments in the MICRO-AIR dosage rate. Adjustments to the dosage should be based on the amount of entrained air in the mix at the point of placement.
5. MICRO-AIR admixture should be stored and dispensed at 35° F (2° C) or higher. Although freezing does not harm this product, precautions should be taken to protect it from freezing. If it freezes, thaw and reconstitute by mild mechanical agitation. Do not use pressurized air for agitation.
6. **CAUTION:** MICRO-AIR admixture is a CAUSTIC solution. In case of contact with skin, eyes or clothing, immediately flush the exposed area with water for at least 15 minutes. Remove contaminated clothing and shoes. Call a physician—especially if contact is with eyes. Wash clothing before reuse and discard shoes. Always keep the product out of the reach of children.

PACKAGING:

MICRO-AIR admixture is supplied in 55 U.S. gallon (208 litre) drums and bulk delivery.

For suggested specification information or for additional product data on MICRO-AIR air-entraining admixture, contact your local Master Builders representative.

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chloride-based accelerators suspect or entirely banned by many agencies, not only for reinforced and prestressed concrete, but for pavement concrete as well.

Generally speaking, admixture manufacturers have divided accelerators in "chloride-based" (primarily calcium chloride), and "non-chloride" based accelerators, and often advertise non-chloride based accelerators without specifying the active agent being used. Users tend to make the reasonable assumption from this that non-chloride accelerators are all about the same or at least similar to each other in their effects in concrete. This is very far from the truth.

Calcium nitrite is an effective concrete accelerator, but it also has the very desirable property of acting as a steel corrosion inhibitor. It is marketed by at least one firm as a corrosion inhibitor, with the concrete acceleration properties being incidental.

Other non-chloride accelerators market include products based on calcium formate, and especially in complex admixtures, triethanolamine. Little triethanolamine is used by itself. A variety of other organic and some inorganic compounds have been listed in the literature as having accelerating properties but are rarely used in commercial practice.

Sodium thiocyanate based accelerators have been marketed by at least one company. However, their use has been questioned for concrete containing steel, on the basis of possible increased susceptibility of the included steel to corrosion. The question is controversial since evidence has been presented by the manufacturer that at the low dosage rate specified sodium thiocyanate based admixtures did not deleteriously affect the corrosion rate or the time to corrosion.

Non-chloride accelerators tend to be fairly expensive and require relatively high dose rates. A considerable potential market would seem to exist for an inexpensive compound that would act as an effective accelerator without deleteriously affecting other properties of the concrete.

An illustrative product sheet is provided as Figure 3. This sheet is from a manufacturer who stresses the availability of several different formulations, including calcium chloride, calcium chloride blended with corrosion inhibiting components, and a chloride-free accelerator; thus the user may make his choice depending on circumstances (and budget!).

Retarders

Chemical admixtures to retard the setting of concrete constitute a major class of admixtures. Some admixtures for accomplishing this are specified as "Type B" or

	RELCRETE ACCELERATORS Ac ACCELERATORS	RELCRETE ACCELERATORS AcP ACCELERATORS	RELCRETE ACCELERATORS AcN ACCELERATORS
DESCRIPTION	RELCRETE Ac is a concentrated, complex blend of set accelerating and strength enhancing components including calcium chloride. It is highly resistant to freezing in storage.	RELCRETE AcP is a concentrated, complex blend of set accelerating and strength enhancing components including calcium chloride and two corrosion inhibiting components.	RELCRETE AcN is an accelerating admixture formulated from a blend of accelerating components. Chlorides are not used in the manufacture of RELCRETE AcN.
FEATURES	RELCRETE Ac is a very cost effective admixture compared to other accelerators.	RELCRETE AcP is also very economical while providing positive safeguards against corrosion of steel reinforcement.	RELCRETE AcN offers optimum acceleration of setting time and early strength development from a non-chloride formulation.
APPLICATION	RELCRETE Ac is recommended for use in concrete where acceleration of setting time and/or early strength development is required. RELCRETE Ac is not recommended for use in prestressed concrete nor for concrete in potentially aggressive environments.	RELCRETE AcP is recommended for use in concrete where acceleration of setting time and/or early strength development is required. RELCRETE AcP is not recommended for use in prestressed concrete nor for concrete in potentially aggressive environments.	RELCRETE AcN is recommended for use in all concrete applications, including prestressed concrete and concrete to be placed in potentially aggressive environments.
DOSAGE	The recommended range for RELCRETE Ac is 10 to 30 ounces per 100 pounds of cementitious material. Required dosage rate will be influenced by cement and fly ash chemistry and ambient conditions.	The recommended dosage range for RELCRETE AcP is 10 to 30 ounces per 100 pounds of cementitious material. Required dosage rate will be influenced by cement and fly ash chemistry and ambient conditions.	The recommended dosage range for RELCRETE AcN is 15 to 40 ounces per 100 pounds of cementitious material. Required dosage will be influenced by cement and fly ash chemistry and ambient conditions.
REINFORCED CONCRETE	In all reinforced concrete mixes, the concrete should be properly compacted and the concrete cover to reinforcement must be adequate as specified by ACI 318.		

Figure 3. Product sheet describing several different accelerators marketed by a particular manufacturer for different purposes.



RECOMMENDED CONCRETE PRACTICES	
COLD WEATHER CONDITIONS Concrete should not be placed if ambient temperatures are expected to remain below 40°F unless concrete temperatures can be maintained above that level. Concrete should not be placed in frozen forms, even when accelerating admixtures are used, as concrete slawork placed on frozen ground may take many hours to reach initial and final sets. Additionally, strength gain may be adversely affected.	CURING Proper concrete curing practices are essential for obtaining optimum concrete performance. Sufficient moisture and favorable temperatures must be maintained in order for the concrete to develop desired properties. This is especially important during the first seven days.
WINDY CONDITIONS Cracking caused by plastic shrinkage due to high rates of evaporation may be controlled by the following methods: • Erection of windbreaks • Use of fog sprays or other suitable curing methods • Use of suitable admixtures	QUALITY CONTROL Recommended ACI or NRMCA procedures should be followed for the addition of materials, mixer cycle time and plant slump control. Plant control should also include frequent air checks in accordance with ASTM C-173 or C-231.

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512-341-6182

SOUTHERN REGION

Atlanta, Georgia
404-955-0089

CORPORATE OFFICE

San Antonio, Texas
512-349-4069

SOUTHEASTERN REGION

Auburndale, Florida
813-967-6626

MID-ATLANTIC COAST REGION

Greensboro, North Carolina
919-375-4066

MONEX RESOURCES offers a full range of admixtures and fly ash for the ready-mixed concrete and concrete product industries. In addition, custom and specially formulated products are available outside the advertised range.

NOTE: The information contained in this data sheet is to the best of our knowledge true and accurate; but as we cannot control the final use of the product, there are no warranties expressed or implied regarding the product's use or performance. Persons receiving this information should make their own tests to determine the suitability thereof for their particular purpose.

"retarding" admixtures in the ASTM C- 494 specification. There is a considerable degree of overlap with Type D admixtures, which are water-reducing retarders. Indeed, most substances used as retarders are also intrinsically water-reducers in the sense that they are surface active and reduce the water demand. For example, of the various classes of substances that were said by one authority to be commercially used as retarders (lignosulfonates and their derivatives, hydroxycarboxylic acids and their salts and modifications, sugars and other carbohydrates, and heptonates related to sugars and starches), only sugars and other carbohydrates were said not to have intrinsic water reducing properties.

A considerable number of inorganic acids and salts, especially those whose calcium salts are insoluble and form films around cement particles, also act as retarders. However, for various reasons they are not much used in practice.

Unlike accelerators which provide some acceleration of both setting and strength gain after setting, retarders function primarily as set control agents. They are of course used mostly in hot weather to overcome the rapid setting pattern that is a natural feature of high ambient temperature. Retarders are particularly helpful in lengthening the permissible period after batching that vibration can be used, and in avoiding cold joints by enabling adjacent layers to be vibrated into each other.

ASTM C-494 requires Type B retarders to increase initial set time at least 1 hour and not more than 3-1/2 hours, and to increase final set time not more than 3-1/2 hours. Compressive and flexural strengths after 3 days are required to be at least 90% of the control concrete, and there are restrictions on the amount of increase in shrinkage that may be induced. Despite the fact that retarders are most commonly used at high ambient temperatures, the time of setting measurements are specified to be carried out at 73° F.

Water Reducers

Water reducing admixtures (Type A in the ASTM C-494 classification) are designed to reduce the water demand of a given concrete mix while at the same time not markedly influencing other characteristics such as air entrainment behavior or setting time. The action is often described as a "plasticizing" action, and accordingly, water reducing admixtures are sometimes called plasticizers. The specific admixtures marketed under this category, however, have only a limited water-reducing effect at dosages that can be used, and ASTM C-494 requires that only a 5% reduction in water demand be demonstrated. A newer category of chemical admixtures that are much

more effective in reducing water demand, the so-called superplasticizers or high-range water reducers (HRWRs) are designated as Type F admixtures. These must provide at least a 12% reduction in water demand to meet the specification requirement.

Nearly all, if not all, of the surface active materials used as water reducers also have some retarding action. To accommodate the desire for the plasticizing effect without at the same time causing extensive retardation, most commercial water reducers are compound admixtures, in which an accelerating agent is included to compensate for the retardation caused by the active plasticizing chemical. In past years, chloride-bearing accelerators were commonly used; currently, because of the growing sensitivity of many agencies to incorporation of any chloride in concrete, a non-chloride accelerator, usually triethanolamine, is often used. If large amounts of accelerator are used, an accelerating water-reducing admixture can be produced.

In addition to the water-reducing effect, ASTM C-494 Type A admixtures are required to maintain both initial and final set times to not more than 1 hour earlier and 1-1/2 hours later than those of the control concrete. The water reduction is required to effect a compressive strength increase of 10% over the control concrete at 3, 7, and 28 days. Long term compressive strengths and flexural strengths at any age must be at least equal to the controls. A limited increase in shrinkage is tolerated.

Commercial water-reducing admixtures are generally formulated from one or more of a restricted class of materials: lignosulfonates, hydroxycarboxylic acids, and hydroxylated polymers of various kinds. However, many other substances have been reported to have similar effects.

Lignosulfonates are derived from the sulfonation of wood pulp, and tend to be relatively high molecular weight polymers of complex and ill-defined molecular structure. Wood sugars of various kinds are usually present. Since these sugars would induce excessive retardation, they are usually removed from lignosulfonates used as Type A water reducers. Lignosulfonates also tend to entrain air, and an air-detraining agent is sometimes incorporated into the final admixture.

Hydroxycarboxylic acids used in water-reducing admixtures include citric, tartaric, mucic, gluconic, salicylic, heptonic, and malic acids. Unlike lignosulfonates, these tend to be pure chemicals. They are generally used in the form of sodium salts, which are very soluble, and they tend to have a considerable retarding action at higher dosage levels.

Hydroxylated polymers used in water reducers are usually partially-hydrolyzed polysaccharides derived from corn starch or other naturally occurring sources. They are

hydrolyzed to relatively low molecular weights, and do tend to exert a retarding action in addition to their water-reducing effect.

The term "water-reducer" is something of a misnomer. The admixture may usefully be incorporated into concrete without changing the water content, so as to increase the fluidity or workability of the mix. The slump increase produced is a function of the dosage level. Over the usual range and with properly designed concrete, a given dosage will produce about the same slump increase regardless of the initial slump of the concrete to which it is added. For a given dosage, hydroxycarboxylic acid - based water reducers are slightly more efficient than lignosulfonate - based water reducers.

The increase in workability is usually partly lost during the hour or two after mixing. Notwithstanding that the slump loss over time with plasticized concrete is usually greater than without admixture present, the residual slump at any given time is generally greater.

When the mix is redesigned to take advantage of the reduced water demand, the effectiveness of the plasticizer depends somewhat on the specific mix. Greater water reductions are possible at lower cement contents (greater aggregate : cement ratios); at higher original slumps; and if delayed addition is used.

A typical product sheet for a water-reducing admixture is provided as Figure 4. The manufacturer here claims superior finishing characteristics as well as the specified water reducing effect.

Water-Reducing Retarders

Water-reducing and retarding admixtures are classified as Type D admixtures in the ASTM C 494 specification. Paradoxically, since most water reducing admixtures do have retarding effects, these dual-purpose admixtures may be in fact simpler substances than single-purpose admixtures that are supposed to only retard set.

Many water reducing retarders are based on lignosulfonates; generally they contain high sugar contents, to help provide the requisite retarding action. Water-reducing retarders based on hydroxycarboxylic acids and on hydroxylated polymers are also commonly used.

The ASTM functional requirements for this type of admixture separately address the water reducing and the retarding functions. The water demand must be reduced at least 5% compared with the control concrete. The retardation effect is required to result in initial setting between 1 hour and 3-1/2 hours later, and final setting not more than 3-

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CHEMICAL DIVISION

PRODUCT BULLETIN

PSI® 400N

DESCRIPTION

PSI 400N is a normal setting, highly concentrated, multi-component, liquid water-reducing admixture for use in concrete. PSI 400N reduces the quantity of mixing water required to produce concrete of a given consistency while providing greater economy for a given strength. It increases strengths and significantly improves watertightness, workability and finishing characteristics.

PSI 400N water-reducing admixture is compatible with air-entrained or non air-entrained concrete mixes but does not of itself increase air significantly. Specifiers and users of PSI 400N admixture can be assured of superior results in both the plastic and hardened state of all concrete. Its superior finishing characteristics provide concrete that is free from blemishes, pitting and other undesirable surface defects. PSI 400N is manufactured in our own plants under rigid quality control standards.

ADVANTAGES

PLASTIC CONCRETE

- Reduces mixing water for given consistency
- Improves workability
- Reduces segregation
- Improves placing and finishing characteristics
- No effect on setting time

HARDENED CONCRETE

- Increases compressive, flexural and bond strength
- Reduces cracking and shrinkage
- Reduces permeability—increases watertightness
- Increases resistance to freezing and thawing
- Provides improved finished appearance
- Reduces bleeding (ASTM C-232)

APPLICABLE STANDARDS

ASTM C-494 Type A
CRD C-87

TECHNICAL DATA

DOSAGE RATE

3-4 fl. oz. per 100 lbs. cement

TYPICAL COMPRESSIVE STRENGTH (psi)

5½ sacks cement per c.y.

Tested at same slump

	PSI 400N		
	Plain	3 oz.	4 oz.
7 days	3000	3550	3700
28 days	4580	5250	5500

TYPICAL INITIAL SET TIME

5.5 sacks cement per c.y.

Tested at same slump

PLAIN — 4½ hours

PSI 400N @ 3 oz./100# cement —
4½ hours

PSI 400N @ 4 oz./100# cement —
5¼ hours

COMPATIBILITY

PSI 400N is compatible with air-entrained cements and all approved air-entraining agents. Also compatible with calcium chloride and stearates.

PRECAUTIONS

PSI 400N can be dispensed at temperatures as low as +23 degrees. Care should be taken to prevent freezing below this temperature; however, freezing does not damage the material if subsequently agitated after thawing.

PSI 400N, being chloride-free, is recommended for prestressed concrete, concretes containing dissimilar metals, and all other uses.

TECHNICAL SERVICES

A trained Gifford-Hill representative is available to all specifiers and users to assist and advise in specifications, dispenser installation and field service.



MOUNTAIN CREEK TOLL BRIDGE, Dallas, Texas
Texas State Department of Highways and Public Transportation
J. D. Abrams, General Contractor

Figure 4. Product sheet describing a water-reducing admixture. Other benefits are also claimed for this product.

1/2 hours later than the control concrete. The limitations on the effects on strength and shrinkage are the same as those for Type A water-reducing admixtures.

Use of a single admixture for both the water-reducing and retarding effects has the obvious advantage of simplicity. However, the balance between the two functions is not easily tailored for particular situations. One can increase the dosage, which will lead to both additional retardation and additional water reduction, or decrease it and undergo reductions in both effects. Nevertheless as a practical matter, water reducing retarders are widely used and generally work well. They tend to be relatively inexpensive.

Occasionally water-reducing retarders are implicated in false-setting problems, and their use with cements that tend to be false setting should be carefully monitored. What appears to happen is that the admixture coats the interground hemihydrate in the cement sufficiently to interfere with and slow down its usual rapid conversion to gypsum. The gypsum formation may be delayed until after the usual mixing cycle. A thickening and in extreme cases, a false setting effect is produced that interferes with proper concrete placement. Usually a second mixing or an extended mixing will cope with this effect.

A product sheet for a polymer-type water-reducing retarder is provided for illustrative purposes as Figure 5.

Water-Reducing Accelerators

These admixtures, unlike most water-reducing retarders, are formulations containing a substantial amount of separate set-modifying, i.e. accelerating, component. This is necessary to overcome the intrinsic retarding effect and then provide the desired additional accelerating effect.

These admixtures are classified as Type E in the ASTM C-494 specification. The specific functional requirements combine those for Type A (water-reducing) and Type C (accelerating) admixtures. The late strength requirements are those of Type A.

Unlike water-reducing retarders, this category of admixtures is relatively little used in practice. The need to regulate the degree of acceleration needed to overcome cold-weather or other problems is perhaps more difficult to satisfy in a combined admixture.

An illustrative product sheet is provided for an admixture of this type as Figure 6. Note that the manufacturer stresses that the acceleration is accomplished using a non-

Plastocrete 161R
Polymer-type, water-reducing,
set-retarding admixture

Description: Plastocrete 161R is a polymer-type admixture. It is a non-air-entraining, water-reducing, set-retarding admixture. Plastocrete 161R contains no chlorides. It meets the requirements of ASTM C-494 Type D.

Where to Use: Use where retardation is needed. Use where high strength, cost-effective concrete is needed. Use where increased workability is needed. Use in mixes with a reduced cement content. Use in all concrete where high quality is required.

Advantages: High structural quality concrete. Saves cement... equal strengths with $\frac{1}{4}$ to 1 sack/cu yd reduction in cement. Higher strength...20% higher compressive strength with equal cement. Set-retarding...initial set will be retarded approximately 20-40%. Increases workability. Contains no chlorides.

Dosage: 3-5 fl oz/100 lb cement.

Packaging: 5-gal pails, 55-gal drums, and bulk.

Shelf Life: Unlimited. Protect from freezing.

Storage Conditions: Store above 30F. Protect from freezing. If frozen, thaw and agitate before using.

Color: Dark brown.

Mixing: Add correct amount of Plastocrete 161R at the concrete plant. Add manually or by automated dispenser directly into sand at weigh hopper or into the water line at the batch plant.

Limitations: Do not mix with air-entraining agent. Protect from freezing.

Caution: See product label, Material Safety Data Sheet, Tech Data Sheet, or contact Technical Service Department.

Figure 5. Product sheet describing a water-reducing set-retarding admixture, marketed by the Sika Corporation.


Fosroc®

CONPLAST NC

Chloride free, accelerating, water reducing admixture.

USES

To accelerate the setting and early strength gain of Portland Cement concrete and mortar mixes without the introduction of chloride.

Acts as a plasticiser, giving significant increases in both ultimate and early strengths. Typical applications include precast concrete, concrete placed in cold weather, concrete for repairs and mortars for brickwork.

ADVANTAGES

Chloride Free:	Safe with all prestressed and steel reinforced concrete.
Anti-frost:	Early setting provides improved resistance to frost attack and earlier finishing.
High Early Strength:	Reduces form stripping time.
Water Reducing:	Plasticizing action facilitates water reduction and increased ultimate strengths.
Versatile:	Can be used with all types of Portland Cement and equally with all concrete and bricklaying mortar mixes.
Low Temperature Use:	Particularly effective in concrete at low temperatures. Allows continued placing of concrete. Enhances cold weather concrete applications by reducing the water content and accelerating hydration of cement.

DESCRIPTION

CONPLAST NC is an admixture designed for use with every type of Portland Cement. It is guaranteed completely free of all forms of added chloride and is supplied as a light straw colored liquid instantly dispersible in water.

The main active ingredient is an inorganic formate.

The addition of the material to Portland Cement concrete and mortar mixes reduces setting times and accelerates the rate of strength gain and resistance to frost attack.

CONPLAST NC is also a plasticizer which, where required, enables the water/cement ratio to be reduced while still maintaining workability. Such reduction will result in significant increases in both ultimate and early strengths.

STANDARDS

CONPLAST NC complies with the requirements of ASTM specification C494 Type C.

PROPERTIES

Calcium Chloride Content: Nil

Specific Gravity: 1.27 at 70° F.

Freezing Point: -3° F.

Air Entrainment: Less than 1% additional air is entrained.

Compatibility: May be used with all types of Portland Cements complying with ASTM specification C150. Not suitable for use with high alumina cement.

The effects of CONPLAST NC are highly effective with Portland Cement mortar mixes. This avoids the use of chloride in brickwork while providing early strength and frost resistance.

CONPLAST NC is generally compatible with other FOSROC admixtures, however, they should always be dispensed separately.

Setting Time: The addition of CONPLAST NC to Portland Cement concrete mixes accelerates both the setting and rate of strength gain.

Compressive Strength/Density: Accelerates the rate of strength gain.

The strength improvements are most significant during the first 18 hours. If no change is made in the water/cement ratios, the ultimate strengths will be similar to those obtained using the same mixes without CONPLAST NC.

FOR MORE TECHNICAL INFORMATION 1-800-841-0445

Figure 6. Product sheet describing a water-reducing accelerating admixture. The accelerating component is said to be an "inorganic formate" and the admixture is said to be free of chloride.

Durability: Accelerated corrosion testing of steel in concrete has shown that CONPLAST NC does not affect the protection of steel afforded by cement against corrosion, even at 4 times the recommended dosage level.

INSTRUCTIONS FOR USE

Dosage:

The optimum dosage for standard concrete and mortar mixes with all grades of Portland Cement is best determined by site testing.

As a guide, the rate of addition is generally in the range of 30-45 fl. oz./100 lbs. of cement.

Overdosing:

An overdose of double the recommended amount of CONPLAST NC will result in a slight increase in initial acceleration, but will not alter the ultimate strength or characteristics of the cured concrete or mortar.

Dispensing:

The correct quantity of CONPLAST NC should be measured by means of a recommended dispenser. FOSROC'S Technical Department should be consulted regarding suitable equipment and its installation.

The measured quantity of CONPLAST NC should be added directly into the mixer. Best results are obtained when added at the same time with the mixing water or at the end of the batch cycle.

When the air temperature, at placing, is below 50° F ACI 306 recommended practice for cold weather concreting should always be followed.

STORAGE

CONPLAST NC has a minimum shelf life of 12 months providing the temperature range does not exceed 10° F. to 125° F. If these conditions are exceeded FOSROC should be contacted for advice.

PACKAGING

CONPLAST NC is supplied by bulk delivery or in 55 gallon drums.

WARRANTY

Fosroc warrants its products to be free of defects in material and workmanship. Under this warranty, we will provide, at no charge, product in containers to replace any product proved to be defective when applied in accordance with our written instructions and in applications recommended by us as suitable for this product.

All claims concerning product defects must be made within 12 months of manufacture. Absence of such claims in writing during this period will constitute a waiver of all claims with respect to such product.

This warranty is in lieu of any and all other warranties express or implied and Fosroc shall have no other liability of any kind including liability for consequential damages.



FOSROC INC.
(Formerly Preco and Caltite CPD)
55 SKYLINE DRIVE
PLAINVIEW, NEW YORK 11803
516-935-9100 - FAX: 516-935-9143

ST NC USA/1-86/BOW

chloride accelerator (an "inorganic formate"), and is therefor safe for prestressed and steel reinforced concrete.

High-Range Water Reducers (Superplasticizers)

The development of this class of chemical admixtures has marked a considerable revolution in the concrete field. In particular the availability of superplasticizers, used in conjunction with silica fume and fly ash, has made possible the development of a whole new class of high-performance concretes. Superplasticizers can be, and are, used in more conventional concretes, and in this section uses with conventional concretes are discussed. High performance concretes will be discussed in a special section later in this report.

Superplasticizers are specified as Class F admixtures in the ASTM C-494 scheme. The operational requirement is that a water reduction of at least 12% be achieved. The reduction in water content is required to produce compressive strength increases of at least 40% at one day, with progressively lesser increases required at later ages. At 6 months and later, the compressive strength is only required to match that of the control concrete. Only a modest flexural strength effect is required, the only increase specified being 10% at 3 days.

The specification also includes requirements of only modest changes in set time and modest shrinkage increases; these are identical to the corresponding requirements for water reducers.

None of the water reducers discussed previously, with the possible exception of a few modified lignosulfonate products, can be used in concrete at high enough dosages to meet the performance required from superplasticizers; retardation, air entrainment, and possibly other undesired side effects interfere. Rather, superplasticizers generally speaking, represent entirely new chemical classes of admixture. Two families are commonly recognized; those based on naphthalene sulfonate and those based on melamine sulfonate, with the former far more commonly used. Actually, at least one admixture company has provided a superplasticizer blend containing both, and has claimed certain advantages for such a blend.

"Naphthalene sulfonates" are actually naphthalene formaldehyde sulfonic acid salts. They are produced by sulfonating naphthalene, polymerizing or "condensing" the sulfonated naphthalene with formaldehyde, and then neutralizing the sulfonate groups on the resulting polymer backbone with Na or Ca. Optimal chain length of the polymer

is of the order of 10, but commercial products contain varying chain lengths, and often some sodium sulfate (if Na-neutralized.).

"Melamine sulfonates" are sulfonated melamine formaldehyde salts, produced by a rather more complex process, and are of a much higher degree of polymerization, on the order of 100 or so. These materials were actually developed for other purposes, and subsequently were found useful in concrete. In contrast, naphthalene sulfonates were a later, and deliberate development for use in concrete.

The general effects of the two classes of superplasticizer are markedly similar to each other. Both act as strong deflocculants, converting the fresh cement paste into a Newtonian fluid of relatively low viscosity. There is usually strong absorption of the superplasticizer by the earliest cement hydration products, often leading to an inadequate later concentration and pronounced loss of the dispersive effect, manifested as slump loss. Delayed addition of at least some of the superplasticizer tends to combat this effect.

In research reported in Part II of this final report, it has been shown that the effect of the superplasticizer is dependent on such cement characteristics as alkali content, the form of the interground gypsum compound, and other factors.

As with water reducing admixtures, superplasticizers may be used either to produce more fluid concrete (when the water content is not changed), or much stronger concrete, if advantage is taken of the water demand reducing effect to actually lower the water content. Obviously intermediate effects can be obtained by partial reductions in water content.

Because of the higher dosages that can be (and are) used, the superplasticizers tend to have quantitatively much greater effects than water reducers. They can be readily used to produce "flowing concrete". Such concrete is almost entirely self-compacting concrete of extreme slump, but produced at normal water contents, and generating normal or greater than normal strengths. ASTM provides a separate specification (C 1017 - 90) to cover superplasticizers intended for such use.

While superplasticizers can be and are used at much higher dosages than conventional water-reducing admixtures, the dose-response relationship for plain concrete is such that increased dosage beyond some particular level (of the order of 1% or 2% of the weight of the cement) has little marginal effect. Once the cement is fully deflocculated, little further increase in response can take place.

The ASTM C 1017 - 90 specification ("Standard Specification for Chemical Admixtures for Use in Producing Flowing Concrete,") recognizes Type I ("plasticizing") and Type II ("plasticizing and retarding") admixtures as separate types. Both types are

required to produce at least a 3 -1/2 inch increase in slump and compressive and flexural strength levels of at least 90% of the reference concrete at all ages. The superplasticizing admixture is required to have only minimal effect on the setting time.

Flowing concrete, as might be expected, tends to have a tendency to bleed and segregate as the result of the loss of "body" in the fresh concrete. This can usually be counteracted by appropriate adjustment on the mix design, especially by increasing the proportion of fine sand.

For applications in which higher strength rather than flowing concrete are desired, the extent of water reduction obtainable can be very much higher than the 12% minimum value specified in ASTM C-494. At high dosage levels, water reductions up to about 30% can be obtained with many naphthalene sulfonate or melamine sulfonate type superplasticizers, especially if they are added after a few minutes delay. Very much increased strengths can be produced at these lower water contents, even without going to silica fume or fly ash additions.

It is of course possible to use superplasticizing admixtures to reduce the cement content, i.e. by maintaining a constant or nearly constant water:cement ratio as the water demand is reduced. This of course results in an increased proportion of coarse and fine aggregate. Sometimes only the coarse aggregate content is allowed to increase. The resulting economy can partially offset the extra cost of the superplasticizer.

A illustrative product sheet for this class of admixture is provided as Figure 7.

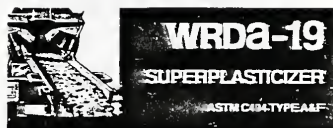
High-Range Water Reducing and Retarding Admixtures

These admixtures, classified as Type G in the ASTM C 494 classification, combine both superplasticizing and retarding effects, usually by blending a naphthalene or melamine sulfonate superplasticizer with a conventional retarder. The functional requirements combine the retarding action requirements specified for Type B retarders with the at least 12% water reducing action specified for superplasticizers. Because of the retardation, the 1-day strength requirement for superplasticizers (at least 140% of the control concrete) is reduced to 125% of the control concrete.

Usage of such admixtures appears to be relatively restricted compared to the usage of non-retarding superplasticizers, although this may change in the future.

An illustrative product sheet describing a specific product falling into this class of admixture is provided as Figure 8.

GRACE · CONCRETE ADMIXTURES



DESCRIPTION:

WRDA-19 is a high range water-reducer, commonly referred to as a superplasticizer. It is an aqueous solution of a modified naphthalene sulfonate. It is a low viscosity liquid which has been formulated by the manufacturer for use as received. WRDA-19 contains no added chloride. WRDA-19 is formulated to comply with specifications for Chemical Admixtures for Concrete, ASTM Designation: C-494 as a Type A, or as a Type F admixture.

One gallon of WRDA-19 weighs approximately 10 lbs.

DISPERSION:

WRDA-19 is a superior dispersing admixture having a marked capacity to disperse the cement agglomerates normally found in a cement-water suspension. The capability of WRDA-19, in this respect, exceeds that of normal water reducing admixtures.

USES:

WRDA-19 produces concrete with extremely workable characteristics referred to as high slump, flowing concrete. WRDA-19 also allows concrete to be produced with very low water/cement ratios at low or normal slumps.

WRDA-19 is ideal for use in prestress, precast, bridge deck or any concrete where it is desired to keep the water/cement ratio to a minimum and still achieve the degree of workability necessary to provide easy placement and consolidation. WRDA-19 will also fluidize concrete making it ideal for tremie concreting or other applications where high slumps are desired.

ADVANTAGES:

1. WRDA-19 can produce high slump flowable concrete at no loss in strength.
2. WRDA-19 can produce low water/cement ratio concrete and therefore, high strengths.
3. WRDA-19, in prestress/precast work, can be used to substantially reduce or eliminate the high energy requirements of external heat for accelerated curing.
4. WRDA-19 concrete produced with Type I cement may be substituted for normal concrete produced with Type III cement to achieve early release strengths.

5. WRDA-19 concrete, even at high slump, exhibits no significant segregation in comparison to concrete without a superplasticizer at the same slump.

6. WRDA-19 aids in rapid discharge of concrete from truck mixers thereby reducing on the job time and improving mixer utilization.

ADDITION RATES:

Addition rates of WRDA-19 can vary with type of application, but will normally range from 6 fluid ounces to 20 fluid ounces per 100 lbs. of cement. In most instances the addition of 10 to 16 fluid ounces per 100 lbs. of cement will be sufficient. At a given water/cement ratio, the slump required for placement can be controlled by varying the addition rate. Should job site conditions require using more than recommended addition rates, please consult your Grace Representative.

COMPATIBILITY:

In concrete containing WRDA-19, the use of a Vinsol resin air entraining agent (such as DARAVAIR®) is recommended to provide suitable air void parameters for resistance against freeze-thaw attack.

Most Type A water reducers or Type D water reducing retarders are compatible with WRDA-19 as long as they are separately added to the concrete. Pretesting of the concrete should be performed to optimize dosages and addition times of these admixtures. Caution should be exercised when using WRDA-19 together with a retarder, as excessive retardation can occur if the admixture dosages are too high. Pretesting of the concrete should be performed to determine dosages and addition times of these admixtures. The admixtures should not contact each other before they enter the concrete.

PACKAGING:

WRDA-19 is available in bulk, delivered by metered tank trucks, and in 55 gallon drums. WRDA-19 contains no flammable ingredients.

It will begin to freeze at approximately 32°F, but will return to full strength after thawing and thorough agitation.

In storage, and for proper dispensing, WRDA-19 should be maintained at temperatures above 32°F.

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DC-8

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Construction Products

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Figure 7. Illustrative product sheet for a high-range water reducer (superplasticizer).



TECHNICAL DATA

EUCON 537
HIGH RANGE WATER
REDUCING ADMIXTURE

3



The Euclid Chemical Company
APRIL 1988

EUCON 537

High Range Water Reducing Admixture
Retarded Set Type

EUCON 537 is a fifth generation admixture formulated specifically to extend the working time of flowing concrete at temperatures up to 130° F. At normal dosage rates, EUCON 537 complies with the parameters of ASTM C 494 Type G admixture. EUCON 537 has been formulated without any added chlorides and complies with ACI 201 and ACI 318 requirements for minimal chloride content.

WHERE USED

EUCON 537 can be added to the concrete at the ready mix plant or at the jobsite. EUCON 537 is compatible with vinsol resin type air-entraining admixtures and many other admixtures; however, all admixtures must be added separately to the mix. EUCON 537 is recommended for all types of concrete including reinforced, prestressed, high strength, parking structures, industrial slabs, watertight concrete and lightweight concrete.

ADVANTAGES

1. EUCON 537 produces "flowing" concrete with controlled delay of slump loss and workability.
2. EUCON 537 greatly reduces water requirements.
3. EUCON 537 reduces segregation and bleeding in the plastic concrete.
4. EUCON 537 reduces cracking and permeability of hardened concrete.
5. EUCON 537, when used to produce flowing concrete, significantly reduces concrete placement time and cost.

ENGINEERING DATA

Water content, maximum percent compared to control

Rate of slump loss, 9" slump concrete, at 72° F.

Rate of slump loss, 9" slump concrete, at 90° F.

Compressive Strengths vs. control

1 day	up to 140%
3 days	140-160%
7 days	130-150%
28 days	125-135%

Relative Durability - freeze thaw resistance

70-80%
1/2" to 1" first hr.
1" to 1 1/2" first hr.

98.7%

DIRECTIONS FOR USE

Quantity - EUCON 537 is used at a range of 6 to 32 ounces per 100 pounds cement. When EUCON 537 is added, at a rate of 12 ounces per 100 pounds cement, to a 1" to 3" slump concrete, it will produce flowable concrete with a slump of 7" to 10".

THE EUCLID CHEMICAL COMPANY

1820 S. REDWOOD ROAD

CLEVELAND, OHIO 44110



IN OHIO CALL
1-216-531-9222

OUTSIDE OHIO CALL TOLL FREE
1-800-321-7628

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The Euclid Chemical Company
APRIL 1988



3

EUCON 537
HIGH RANGE WATER
REDUCING ADMIXTURE

Figure 8. Product sheet for a retarding-type high range water reducer.

The slump loss will be gradual up to six hours (6) at a temperature of 72° F. and up to three hours (3) at a temperature of 120° F when proper quantities of EUCON 537 are used. Variations in slump loss and setting characteristics are a function of the amount of admixture used, cement characteristics and the mix design selected. An increase in concrete temperature will cause an increase in slump loss and a decrease in initial set time.

When designing mixes for use with EUCON 537, ACI 211.1 or ACI 211.2 recommendations should be followed. After the initial mix is established, the sand to coarse aggregate ratio would probably be adjusted upward 5% to 15% to compensate for the water reduction expected, and to maintain homogeneity of the "flowing" mix. For "flowing" concrete, charge all concrete materials into the mixer and mix five minutes or 70 revolutions to a 3½" slump or as required by the project specifications. Add EUCON 537 and mix an additional 30 to 60 seconds per yard, and then discharge.

For high strength concrete, (over 6000 psi in 28 days), add EUCON 537 with approximately 80% of the mixing water and mix 5 minutes or 70 revolutions minimum. Add allowable additional water carefully to obtain the right slump and mix for 30 to 60 seconds per cubic yard.

Suggested Quantities per 100# Cement vs. Air Temperatures

80° F.	10-16 oz.	110° F	12-24 oz.
90° F.	10-18 oz.	120° F.	16-32 oz.
100° F.	12-20 oz.	130° F.	20-32 oz.

FORMWORK

Forms for walls or narrow sections must be watertight, strong, and have good bracing. During the "flowing period" when the concrete is at a slump of 7"-10", the concrete will exert a higher pressure at the base of the form than conventional concrete. Formwork for slabs is the same as for conventional concrete.

PLACING

Concrete with EUCON 537 will spread up to 15' when discharged from the chutes of mixer trucks. A 10 yd. load of concrete can be easily emptied in less than five minutes at the rate of 80 cubic yards per hour.

Concrete will flow down a slope of 5° and in some cases, with extension chutes, it can be discharged direct from the mixer trucks a total distance of 40 to 45 feet.

CAUTION

The use of EUCON 537 varies with every application. Therefore, the Engineering or Technical Services Department of The Euclid Chemical Company should be consulted concerning its use.

To prevent rapid loss of workability at concrete temperatures higher than 75° F. or in windy weather, apply the precautionary methods recommended in ACI 305 R-77 report, "Hot Weather Concreting".

Admixtures Not Covered by Existing ASTM Specifications

The chemical admixture types discussed so far are all covered by ASTM specification. This by no means exhausts the list of chemical admixtures used in concrete or promoted for such use. Some additional admixtures are in process of having specifications compiled and approved; others are used without such specification. The chemical admixtures field is in an active state of development, and chemical admixtures to address new functions are being continuously developed and marketed. The admixtures discussed below probably comprise most, but not necessarily all, of the types available for general concrete use. Admixtures for specialized concretes, such as shotcretes, polymer-modified concretes, or calcium aluminate cement concretes, or for grouts, are not considered.

Corrosion Inhibitor Admixtures

The corrosion of reinforcing and prestressing steel in concrete due to chloride ions has been a major problem in the transportation and highway fields. Bridge decks and other concrete bridge elements, and parking garages have been particularly affected.

For a number of years the main preventive measure specified has been the use of epoxy-coated steel. It now appears that this strategy, at least as has been practiced under current specifications, is flawed. Accordingly, new importance is expected to be placed on the use of corrosion inhibitor admixtures in such concretes.

While a number of chemicals possess corrosion inhibition properties, one admixture marketed commercially is based primarily on calcium nitrite. This material, when added at the normal dosage rate, functions also as a relatively strong accelerator. It also normally increases the ultimate strength of the concrete. When the accelerating effect is not desired, for example in hot weather concreting, a suitable retarder may be added to overcome this effect. It is usually recommended that the two admixtures be added separately.

The effectiveness of calcium nitrite has been extensively documented in various FHWA and other studies. One study has suggested the possibility of superior corrosion resistance might be obtained from a mixture of calcium nitrate and sodium molybdate, but such combined corrosion protection admixtures have not been extensively tested.

Calcium nitrite is used at relatively high dosages, of the order of 2% by weight of cement. The dosage level may have to be increased if very high contents of chloride are expected. The increased costs involved are considerable, but where corrosion risks are high, the expected cost is usually considered to be modest in comparison with the expected benefit, even if high dosages are required..

An illustrative product sheet describing a calcium nitrate based corrosion-preventing admixture is reproduced as Figure 9.

More recently, a corrosion prevention admixture based on based on an entirely different system has been introduced by another major manufacturer. This material is a water-based combination of organic amines (to form a barrier film) and esters (to render the cement paste hydrophobic), and is said to prevent or delay corrosion by forming a hydrophobic barrier to chloride and moisture penetration into the concrete.

Antifreeze Admixtures

Antifreeze admixtures are designed to prevent damage due to freezing in fresh concrete, and to permit continued hydration at temperatures less than 32° F. They have been little used in the United States because of concerns connected with their possible influences on corrosion, on alkali silica reaction, and on air-entrainment. However, at least one antifreeze admixture, said to be free of chloride, has been marketed for several years by a major admixture producer in the United States. Its effects have been described in a recent paper, and are said to include acceleration of both setting and strength gain, as well as antifreeze action.

Compounds that have been used for antifreeze purposes include ammonium hydroxide, various calcium and sodium salts (including nitrate, nitrite, and chloride), potassium carbonate, and urea. In a recent study reported by an agency of the U.S. Army Corps of Engineers, sodium and calcium nitrite mixtures and sodium nitrite-potassium carbonate mixtures were found to be particularly effective. Both these mixtures were additionally recorded as having significant accelerating effect, but both increase the alkali burden of the cement. A new antifreeze admixture free of both chloride and alkalis has recently been marketed in Japan, which is said to contain calcium nitrite and nitrate and polyglycol ester derivatives, and thus be free of this additional alkali burden.

Use of antifreeze admixtures may turn out to be an appropriate and cost-effective way to protect transportation-related structures where early freezing cannot be prevented.

Waterproofing Admixtures

Concrete waterproofers are admixtures added in the mix water that are designed to increase the solid-water contact angle of the hardened concrete sufficiently so that the concrete is rendered water repellent, or "waterproofed". These materials are sometimes referred to as "integral" or "internal" waterproofers, to distinguish them from external coatings designed to do the same job. The waterproofing action functions only for water under modest pressures, but renders concrete, once dry, much more difficult to rewet and resaturate. This confers some benefit in freezing and thawing and sometimes in alkali-silica reaction and steel corrosion situations. Waterproofers are also used for architectural concrete, with benefits such as reduced possibility of efflorescence and better surface appearance being claimed. Precast architectural panels are a common application.

Three different classes of waterproofing admixtures are generally recognized: liquid fatty acids (typically mixtures of oleic and other liquid fats); emulsions of waxes of various kinds, and finely divided waxy solids such as calcium or aluminum stearate.

Waterproofing admixtures are much more commonly used in Europe than in the United States, although they are marketed by several admixture producers in this country. No ASTM standards exist. Nevertheless, the possibilities for their use in transportation related structures involving vertical surfaces where appearance is important should not be overlooked.

"Stop-Start" Admixtures

These are novel and highly sophisticated chemical systems designed to permit the setting and hydration of concrete to be stopped on application of one agent and resumed at some later period when the "stopped" concrete is remixed with the second agent. Usually additional fresh concrete must be blended with the "stopped" concrete when hydration is to be resumed.

These systems were developed more as management tools in concrete operations than as admixtures designed to affect the ultimate properties of the hardened concrete. In particular, they have been marketed as an environmental tools to reduce or eliminate the volume of waste concrete and concrete washings that result from ordinary concrete operations, especially transit-mixed operations.

"Stop-start" admixtures are marketed by several of the largest admixture manufacturers. The chemistry of the effects produced is not widely understood, and the

chemical systems themselves are not disclosed. There are no existing ASTM standards for this class of admixture.

Alkali Silica Reaction Preventing Admixtures

These fall into the category of potential, rather than actual commercially marketed admixtures, although there are indications that one or more admixture companies might market such a product in the near future.

Alkali silica and to a lesser extent alkali carbonate reactions in concrete have led to a number of serious problems, and pavements and other transportation-related structures are not immune.

Approaches toward prevention by means of chemical admixtures have in the past been concentrated on lithium and barium compounds. There is considerable current interest on lithium compounds, and on several new classes of possible admixtures: sodium silicohexafluoride and modified silanes (alkyl alkoxy silane).

State DOTs that operate in areas where alkali silica reactions have been recognized as serious problems might be well advised to follow developments in this field and consider the use of such admixtures when they have become available.

Shrinkage-Reducing Admixtures

A class of chemical admixtures designed to reduce drying shrinkage by decreasing the capillary tension produced on evaporation of water from the hardened cement paste has been developed and marketed in Japan. These admixtures are organic surfactants, said to be based on alcohol alkylene oxide adducts. It is not known whether or when such admixtures will be marketed in the United States, but they may potentially useful in reducing or eliminating shrinkage cracking in pavements and other transportation - related structures.

SOURCES OF FURTHER INFORMATION

There is a large body of published research information on chemical admixtures. However, the specific manufacturer or brand name is rarely mentioned in research papers, making the information less useful than it might be. On the other hand, where the research was done by a specific admixture company, the brand name might be men-

tioned or easily inferred, but sometimes the objectivity of the results might be called into question.

Unfortunately, primary research sources tend to be relatively unavailable to most engineers associated with state DOTs.

Accordingly, the temptation to provide a long list of paper citations has been resisted. The citations given below are to books, technical compilations, and other sources that provide a condensed body of information, rather than to individual papers.

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MINERAL ADMIXTURES AND HIGH-PERFORMANCE CONCRETE

Mineral Admixtures:

It is customary to divide concrete admixtures in to separate categories of chemical admixtures (the subject of this report), and so-called "mineral admixtures". Loosely, the latter comprise natural and manufactured pozzolans, fly ash, silica fume, and ground granulated blast furnace slag, although the latter is sometimes split off as a cementitious component rather than a mineral admixture.

There are various interrelationships that necessarily develop between chemical admixtures and mineral admixtures when both are incorporated into concrete. In recent years in the U.S., the use of mineral admixtures, especially fly ash, has become almost universal in ready mixed concrete, and very widespread in other concretes, including concrete for transportation related structures and pavements. Slag has recently become more widely available, and its use is greatly increasing, as is silica fume for special structures. Accordingly, chemical admixtures must also be examined as agents that combine with, and interact with mineral admixtures in their joint use in concrete.

A brief synopsis of the composition and relevant behavioral characteristics of common mineral admixtures is provided below.

Natural and artificial pozzolans, in the strict sense, are glassy or amorphous materials, usually highly siliceous, which have been ground to reasonable fineness and are known to function in concrete by relatively slow reaction with the calcium hydroxide de-

veloped in the early cement hydration reactions. Except in a few areas, such materials are little used in the United States.

Fly ashes are very specific materials. All are derived as by-products of the combustion of powdered coal in electrical generating plants, usually collected by electrostatic precipitators (although sometimes by baghouse collectors), and are fine enough by nature so that they are rarely ground. Fly ashes are conventionally divided into ASTM Class F and ASTM Class C categories, the division relating primarily to the calcium content, Class C being richer in this chemical element. The division reflects the nature and calcium content of the coal being burned.

Many, but not all, fly ashes are composed primarily of spherical particles, mostly solid, but some hollow. Coarser particles tend to be "slaggy" and not reactive in concrete. Most fine and medium sized fly ash particles are composite in character, being made up of crystalline components embedded in a glass matrix. In Class F fly ashes, the glass tends to be reactive in concrete, with the incorporated crystalline components (quartz, mullite, iron oxides, etc.) being unreactive. Many Class C fly ashes have reactive crystalline components as well as reactive glass.

Reactions of fly ashes in concrete tend to be slow, especially for Class F fly ashes, and are quite complex. Although ASTM and other agencies classify fly ashes as pozzolans, their effectiveness in concrete stems only partly from reaction with calcium hydroxide; much of the benefit seems to develop as a result of the presence of the fly ash stimulating additional cement hydration reaction.

Fly ashes may contain a greater or lesser contents of unburned carbon, derived from the coal. Additionally, some fly ashes are treated with salts, frequently sodium sulfate or sodium carbonate, in the burning operation so as to render them more readily precipitated in electrostatic precipitators. Such fly ashes retain a significant surface contamination of such salts which may influence the behavior of chemical admixtures. Fly ashes with high contents of high-surface area carbon tend to absorb most organic admixtures, and their presence may require significantly increased dosages to maintain effectiveness.

Silica fume is another very specific material whose characteristics reflect its mode of origin. Silica fume is a byproduct of the manufacture of silicon or sometimes ferrosilicon. In such manufacturing processes silica sand and wood chips (with added iron oxide in the case of ferrosilicon) is subjected to high electrical current. The desired reaction is the reduction of the SiO_2 to Si metal, but in the process some unstable SiO is vaporized and condenses in the surrounding atmosphere to particles of very finely divided siliceous glass. The glassy spheres are collected by baghouse separators, and

depending on SiO_2 content and purity, may have remarkably reactive characteristics in concrete.

Silica fume is also classed formally as a pozzolan. However, like fly ash, its behavior in concrete is conditioned only partly by its ability to combine with calcium hydroxide. Like some fly ashes, it stimulates additional cement hydration, but unlike most fly ashes, it has a remarkable filler effect because of its extreme fineness.

Silica fume is commercially marketed in powder form, and also in slurry form. In slurry form, sufficient superplasticizer is normally added to keep the silica fume particles in the dispersed state. However, for some uses, additional superplasticizer may be required for optimum effect.

Ground granulated blast furnace slag is another very specific material. This material is derived from blast furnace slag produced in the iron industry by a process of water quenching of slag (iron impurities) from the molten state (granulation), and subsequent grinding to cement fineness. Such slags are glassy, but have some crystalline inclusions. The glass is rich enough in calcium that in suitable fineness it can function as a slowly reacting hydraulic cement by itself or with the incorporation of a suitable activator. The hydration reaction generates calcium silicate hydrates not unlike those produced by Portland cements. When used in Portland cement concrete the reactions are more complex, and result in a denser and less porous overall hydrated cement structure; the resulting concrete often develops superior durability characteristics.

High Performance Concretes:

High-performance concretes constitute a catch-all category of concrete that, loosely speaking, includes concretes of much higher strength, and often of much greater potential durability than normal concretes. These favorable characteristics may be attained by a variety of approaches, but nearly all involve simultaneous use of large amounts of both chemical and mineral admixtures.

It appears in particular that superplasticizers, when used in combination with silica fume, develop a synergistic action that results in a much greater effective dispersing action than when superplasticizers are used with plain Portland cement concrete. This permits batching at a very much lower water content than is normally employable. Under favorable circumstances the cement paste developed in the hardened concrete provides a much denser and more favorable coating for the aggregates. The permeability and ionic diffusivity of the hardened concrete are very much reduced. The "transition zones" around the individual aggregate particles are very much improved so

that bond cracking becomes rare, and the overall compressive and flexural strengths may be radically increased.

Similar results can be obtained with certain fine fly ashes instead of silica fume, and with combinations of fly ash and silica fume. The dispersion may be effectively and more economically obtained by combinations of water reducing and superplasticizing chemical admixtures rather than by superplasticizers alone. The alkali content of the cement, its fineness, and the nature of its gypsum component may also need to be controlled.

Because of the exceedingly low water content at which these concretes are batched, little bleeding takes place. The impermeability of the fresh paste makes it very difficult to convey water from the interior to the surface to replace any water lost in early evaporation. In consequence, curing under continuously and effectively wet conditions are absolutely necessary to avoid plastic shrinkage cracking.

Such high performance concretes are exceedingly expensive and do not lend themselves readily to conventional methods of construction. They are not suitable for paving train operations, but compressive strengths in the laboratory in excess of 100,000 psi. These are laboratory curiosities at present, but may point the way to future systems that might have applications in redesigned transportation system structures.

ADMIXTURE COSTS

Decisions on prospective admixture use are not usually taken without some consideration of the costs involved, whether or not a formal cost-benefit analysis is attempted. None of the many literature references cited (including the guides to admixture use developed by committees of the American Concrete Institute and of the Transportation Research Board) attempt to provide cost information.

There are obvious pitfalls in attempting to provide such admixture cost information. Actual costs vary not only with dosage selected, but also with location, with size of the construction operation, and certainly with competitive conditions in the industry. Nevertheless, it is important to have some sense of the costs involved.

I have attempted, with the kind assistance of industry sources, to provide an estimate of the marginal materials cost for each of the kinds of admixtures considered. The calculations have been made in terms of direct admixture cost per cubic yard of

concrete using the approximate average admixture dosage. As the admixture dosage is usually specified in terms of the cement factor of the concrete, a cement factor must be assumed; the costs here are calculated on the assumption of a 517 lb/cu. yd. (5-1/2 bags per cu. yd.) cement factor.

The average price per cu. yd. of concrete in various markets is published periodically by Engineering News Record. Based on these estimates, I have selected a rough figure of \$60 per cu. yd. as representative of the base cost of concrete.

Using these assumptions a good general idea of the costs of the various classes of admixture can be found from the data in Table 1. The second column of Table 1 contains an estimate of the range of cost for the generally recommended admixture dose specified per cubic yard of concrete. The third column is a corresponding calculated percentage increase in concrete cost, using the mean value for the range in Column 2 and a \$60 assumed base cost of concrete

It is apparent that the various admixtures can be divided into only a few classes so far as cost is concerned. The writer considers that marginal costs of 2% or less are trivial; that marginal costs between 2% and 5% are inexpensive; and that admixtures that add between 15% and 30% to the cost of the concrete are relatively expensive. Surprisingly, there seems to be a large gap between 5% and about 15%, i.e. what one might characterize as moderate cost admixtures, do not seem to exist.

With these definitions, it is seen that the cost involved for air entraining agents, chloride-based accelerators, and water reducers are all trivial; that non-chloride based accelerators, superplasticizers, retarding superplasticizers, and water-proofers fall into the inexpensive category; but that corrosion-resisting admixtures, alkali silica reaction preventing admixtures, and the necessary combination of silica fume and high dosage superplasticizer to generate high performance concrete are all in the relatively expensive category.

Table 2. Admixture Cost Estimates

<u>Admixture Type</u>	<u>Cost Per Cubic Yard</u>	<u>Percentage Cost Increment</u>
Air-entraining agents	0.07 - 0.13	0.17
Water-reducing retarders	0.24 - 0.58	0.68
Water reducers	0.25 - 1.05	1.1
Chloride-based accelerators	0.65 - 1.51	1.8
Waterproofers	1.45 - 3.58	4.2
Non-chloride accelerators	2.17 - 3.40	4.6
Superplasticizers	2.40 - 3.75	5.1
Retarding superplasticizers	2.40 - 3.67	5.1
Organic corrosion inhibitors	9.10 - 11.50	17
Calcium nitrite-based corrosion inhibitors	14.00 - 20.00	28
Silica fume + superplasticizer	14.40 - 15.75	25
Alkali silica reaction mitigating admixtures	14.00 - 23.00	31
Anti-freeze admixtures	17.00 - 25.50	35

A PROSPECTIVE ON THE USE OF ADMIXTURES IN CONCRETE USED FOR TRANSPORTATION-RELATED STRUCTURES

Whether to specify or to permit admixture use in particular transportation-related structures, and what admixtures to consider using is a complex technical (and economic) decision that has been often neglected.

In part the decision should be based on the technical requirements of the structure; in part, on appropriate cost-benefit considerations; and in part on questions of familiarity and practicality. In particular, the projected incorporation of several different admixtures in the same concrete often raises concerns about mistakes and over- or under-dosages.

An idea of the costs involved in using particular admixtures has already been provided.

The technical requirements of the structure would normally exercise primary control concerning what, if any, admixtures to incorporate. For example, it is very clear that the benefits of air-entrainment in preventing freeze-thaw damage are so important, that any concrete structure that is exposed to freezing under any circumstances should be air entrained. The fact that the added cost is trivial is welcome, but not governing.

Since bridge decks and other bridge structures are heavily reinforced and exposed to salts or other sources of chloride in most of the United States, and since the mandated use of epoxy coating seems less than completely effective, the incorporation of a corrosion prevention admixture (in addition to the epoxy coating treatment) should certainly be considered despite the relatively high cost involved. Conversely, since most pavement concrete incorporates only load-transfer dowels, such admixtures are obviously not needed and not appropriate.

Many admixtures (such as accelerators and retarders) are primarily processing aids and have comparatively little effect on the properties of the concrete in the final structure. Whether or not they should be used depends on the details of the

construction process itself. To some extent water reducers and superplasticizers fall into this category. It is evident that heavily superplasticized concrete is inappropriate for the usual highway paving train operation because of the extreme change in rheology of the fresh concrete. On the other hand, the ability to place concrete in "flowing concrete" form is extremely beneficial and appropriate for construction requirements on bridge decks, where congested steel and much different placement requirements obtain.

The potential use of alkali silica preventive admixtures is extremely important in certain geographical areas where potentially reactive aggregates dominate and alternatives are few and expensive. Much of the State of Nevada is one such region. Conversely, alkali silica reaction damage in pavement and other structures in the limestone regions of Southern Indiana is practically unknown, and incorporation of such admixtures in concrete in that area is clearly not appropriate.

Some of the admixtures discussed can be used individually or in combination to "upgrade" the concrete; that is to simultaneously provide stronger, less porous, and consequently more durable concrete. In general terms, admixtures that permit placement at lower water contents, such as water reducers and superplasticizers, if used for this purposes and not merely as a processing aid all into this category. Combinations of such admixtures with appropriate kinds of fly ash or silica form are particularly effective and can lead to distinctively "high performance" concretes, as has been discussed previously. The degree to which such usage is appropriate depends very much on the specific concrete structure involved. Obviously low-volume road pavement structures have less need for such superior (and inherently more expensive) concrete than bridge decks and other critical structures. Technical considerations with respect to the construction process to be used also need to be thoroughly understood, especially those involving proper curing for these low water content, inherently impermeable concretes.

Some consideration about potential problems involving the use of multiple admixtures in the same concrete needs to be expressed. Obviously, the simultaneous use of a number of different chemical substances, each of which needs to be batched accurately, in field construction can lead to problems. Surprisingly, there are comparatively few documented indications of serious difficulties due to mutual interactions of different admixtures, but that could change in the future if the use of multiple admixtures becomes more widespread.

Finally, the promise for the future of shrinkage-reducing admixtures should not be overlooked. All concrete structures shrink, and almost all eventually crack by this mechanisms. The effects on pavement integrity of heavy traffic superimposed on shrinkage cracked- concrete is obvious. Should effective commercial admixtures that consistently and reliably prevent shrinkage cracking become available, the potential benefit to pavement structures could be of major importance.

PART II

QUANTITATIVE ANALYSIS OF INTERACTIONS BETWEEN PORTLAND CEMENTS AND SUPERPLASTICIZERS ,

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ABSTRACT

A new approach to studying interactions between chemical admixtures and cements has been developed in this research. Features include repeated analyses at short intervals of physico-chemical parameters important in admixture effects including the sulfate-bearing phases of the cement (gypsum, hemihydrate, and insoluble anhydrite), ettringite, and concentrations of the admixture and of inorganic ions in the paste solution. The gypsum, hemihydrate, and ettringite analyses are made by DSC; anhydrite is analyzed by QXRD; admixture concentrations are measured by UV spectroscopy; and inorganic ion concentrations are measured by conventional methods. The physical behavior of the paste is also monitored.

Studies have been carried out using both naphthalene sulfonate and melamine sulfonate superplasticizer admixtures. The methods developed can be applied for any chemical admixture.

Two different conventional portland cements and a special white cement have been used. The white cement has a very low alkali content, and anhydrite is the single form of calcium sulfate present.

The effectiveness of the superplasticizer has been found to depend on maintaining a reasonable concentration of it in solution. Cement mixes that do not were found to stiffen and set prematurely. This response was found to be associated with a low concentration of sulfate in the paste solution. Adding sulfate reduces the early uptake of superplasticizer and allows the admixture to function properly.

In all cases it has been found that the presence of the superplasticizer modifies the early pattern of ettringite development.

Na^+ ions balancing the negative sulfonate sites in the superplasticizers are immediately detected in the paste solution. As the dissolved polymer is incorporated into the hydrating cement, the sulfonate sites are replaced by OH^- ions, leading to a permanent increase in the OH^- ion concentration.

The early absorption of superplasticizer by the hydrating cement was found to be reversible under some circumstances.

When excessive amounts of alkali hydroxides were added to superplasticized white cement, premature stiffening of a variant kind was developed.

CHAPTER ONE

INTRODUCTION

1.1 General

Admixtures generally have become of major importance in concrete construction recently. Due to multiple purposes of the concrete structure and various restrictions on the construction environments, the requirements for the performance of the concrete have become more varied, and more specific for every construction. In order to satisfying the various demands for concrete, new and different kinds of chemical admixtures have been developed and recently made available. These newer chemical admixtures, such as superplasticizers, offer distinctive advantages over older systems, and appropriate use has been shown in many cases to provide major benefits in terms of both strength development and durability.

However, these benefits of chemical admixtures come at some cost in chemical complexity and possible interaction problems when incompatibilities with certain cement types, mutual incompatibilities among several chemical admixtures, or incompatibilities with other concrete components arise. Chances are higher for these deleterious interactions to take place, because using a variety of cements along with multiple kinds of admixtures at the same time in concrete is not unusual nowadays.

Although research needs for these interaction problems are high, the number of basic studies to investigate the mechanisms of the problem is smaller than that of the practical studies on admixture performance in specific concretes.

Furthermore, the methodologies for studying the effects of chemical admixtures are still to be developed. The additions of chemical admixtures result in various changes in the cement hydration processes, and affect the chemistry of pore solution and solid hydration products. Those changes taking place in time series are visualized by analyzing both organic and inorganic species in the pore solution, and by time-series analyses to show changes in the solid phases. Information obtained by those different analyses are to be integrated and evaluated properly.

Among the various chemical admixtures, benefits of the superplasticizer have become particularly apparent. Since superplasticizers were introduced to the market in 1970's, their excellent performance in obtaining better workability and higher strength in concretes have been widely acknowledged, and the use of superplasticizers become indispensable in advanced concrete construction. Some incompatibility problems with cements have been observed for certain type of superplasticizers, and are considered to be high priority research topics. Superplasticizers are thus considered to be suitable material for an application of the analytical approach.

1.2 Objectives and Scope of Work

The objectives of the research are as follows. First, a comprehensive analytical approach which is suitable for evaluating the interactions between cements and chemical admixtures quantitatively is to be established. This includes the analytical method for determining the admixture concentration levels and their changes with time in cement paste solution, using UV spectrum analysis. Subsequently, the effects of the superplasticizer on the solution phase and the solid phases need to be evaluated in time series by several analytical methods. Especially the analysis of the solids by differential scanning calorimetry (DSC) seemed promising.

In the present work, this analytical approach was applied to the study of two popular types of superplasticizers, naphthalene sulfonate and melamine sulfonate, with three cements. Two of them are ordinary portland cements used in major amounts for concrete constructions in Indiana. Another cement is a white cement, with which a cement-superplasticizer incompatibility problem was observed. The interaction phenomena between these particular cements and superplasticizers were investigated. Finally, the effectiveness and limitations of this experimental approach, and those of the component analytical methods were assessed.

This report consists of nine chapters. An introduction, and the scope of the study are presented in Chapter 1. In Chapter 2, the previous work reported in the literature concerning the interaction between the constituents of cements and admixtures is reviewed and summarized.

The materials used in this research are described in Chapter 3. Chapter 4 provides information on experimental work carried out and on methods used. This includes a summary of the paste mixes prepared and details of the experimental methods used for analyses of the solution and the solid.

In the subsequent three chapters, the experimental results are presented, and discussed. Chapter 5 covers the results on the white cement. In Chapter 6 and Chapter 7, the results on two different ordinary portland cements are presented separately.

In Chapter 8, the previously presented results on three different cements, and those on experimental method itself, are comprehensively discussed. Chapter 9 contains the detailed findings and the overall conclusions.

1.3 Terminology

Some of the terminology used in this study is clarified as follows:

1. Superplasticizers

The term "superplasticizer" is used in this study, as a synonym for the somewhat more clumsy term "high-range water-reducing admixture" preferred by some authorities.

The two types of superplasticizers used in this study have been called by different names by different researchers. The first type has been called variously "naphthalene sulfonate-formaldehyde condensate", "formaldehyde condensate of beta-naphthalene sulfonate", or "sulfonated naphthalene formaldehyde".

However, the term "naphthalene sulfonate" or "naphthalene sulfonate superplasticizer" is used for this type of superplasticizer throughout this study.

The second type has been called "melamine sulfonate-formaldehyde condensate", or "sulfonated melamine formaldehyde" by various authors. However, the name "melamine sulfonate" or "melamine sulfonate superplasticizer" will be used for this type of superplasticizer in this study.

2. Units

The units used in this study are basically SI units, or the units used conventionally in cement chemistry field.

The concentration of all inorganic ions is expressed in milliequivalent per liter, abbreviated as meq/L. 1000 meq/L equals to 1 normality (N). In contrast, the concentration of all superplasticizers is expressed in gram/liter (g/L).

3. Symbol of Oxides

The following abbreviations of the common oxides in the cement chemistry are used throughout the text.

<u>Oxide</u>	<u>Symbol</u>
Al_2O_3	A
CaO	C
Fe_2O_3	F
H_2O	H
SiO_2	S
SO_3	$\bar{\text{S}}$
CO_2	$\bar{\text{C}}$
Na_2O	N
K_2O	K

CHAPTER TWO

REVIEW OF PREVIOUS WORKS

2.1 Cement Paste without Admixture

Prior to discussing superplasticizer performance, some of the literature on hydration of plain cement (without admixtures) is reviewed in this section. Since chemical analysis of the solution phase is one of the primary experimental approaches used in this study, and early responses involving the solid phases containing CaSO_4 is another, these two topics were the focus of the review.

2.1.1 Solution Phase Analyses

With respect to solution phase analysis, an early and comprehensive study was performed by Lawrence [1]. He showed that the major dissolved species were Ca^{2+} , K^+ , Na^+ , SO_4^{2-} , and OH^- , and that relatively high concentrations of these ions were observed early in the hydration. He observed that concentration changes were small for all the ions for the first several hours.

In the solution prior to setting, the concentrations of calcium have been a great concern, especially in relation to the precipitation of the calcium hydroxide phase and thereafter to the hardening. The approach taken frequently was to calculate the degree

of saturation in terms of calcium hydroxide. Hansen and Pressler [2] showed experimental data on the solubilities of $\text{Ca}(\text{OH})_2$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in alkali solution conditioned by different concentrations of KOH and NaOH. At equilibrium, they measured Ca^{2+} and SO_4^{2-} ion concentrations along with those of K^+ and Na^+ . The results show that the Ca^{2+} ion concentration slightly decreases with increasing alkali concentration in the low alkali concentration region. In higher alkali concentration range (higher than about 0.2 N), the Ca^{2+} concentration was not affected by the alkalis. The SO_4^{2-} concentration increases with increasing alkali ion concentrations.

However, Diamond [3] pointed out the importance of the correction for the activities of the ions. With consideration of the activity coefficient and recognizing the importance of the existence of complex ion CaOH^+ in the solution, Gartner et al. [4] indicated that the liquid phase of most cements were supersaturated with respect to CH by a factor of 2 to 3. With respect to gypsum, the degree of supersaturation did not exceed 1.3 in the cases studied.

Bailey et al. [5] tried to develop a computer program to calculate the concentrations of the various species found in the solution and to obtain the ionic activity products of the solutions. They attributed the sudden drop in the ion product of Ca^{2+} and SO_4^{2-} ions observed within the first several minutes of hydration to the formation of secondary gypsum from more soluble forms of calcium sulfates, rather than to the formation of ettringite.

After several hours, the concentration of both the Ca^{2+} and SO_4^{2-} ions decrease suddenly from their plateau levels. Taylor [6] mentioned that this sharp fall corresponded to the renewed growth of ettringite observed in SEM and to the shoulder of the heat evolution curve.

Pore solutions after setting were first expressed in an apparatus described by Longuet et al. [7], and Barneyback and Diamond [8] described the methodology of expressing pore solutions using the apparatus in detail.

Taylor [9] tried to predict the increasing alkali concentration of the pore solution in a long term from the water:cement ratio, total and water-soluble alkali contents of the cement.

2.1.2 Role of CaSO_4 in Cement Paste Hydration

The primary purpose for the addition of CaSO_4 to cements is to slow down the reactions of C_3A , especially when alkalis are present [10]. In calorimetry measurements, the heat evolution curve of pure C_3A hydration in the presence of CaSO_4 shows a pattern similar to that of cement, which shows an intense first peak, an induction period and a second peak of heat evolution. Jawed et al. [11] explained the reason for induction period in this system of hydrating $\text{C}_3\text{A}-\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ system as follows. They stated that ettringite is usually experimentally detected at the surface of the C_3A rather than on the gypsum particles. They considered that ettringite initially forms a coating on the reacting C_3A surface, which slows down the diffusion of inor-

ganic ions (SO_4^{2-} , OH^- , Ca^{2+}), and resulting in slowing down the reaction.

Mehta [12] considered that ettringite formed via a through-solution mechanism rather than via a topotactic mechanism because ettringite formed indiscriminately throughout the system, according to his SEM work.

Tadros et al. [13, 14] presented a view on the retardation of C_3A hydration by the sulfate ion. Using C_3A dissolution data, they concluded that the retardation was not primarily the result of formation of an ettringite film on the C_3A surface but by the adsorption of sulfate ions onto the positively charged C_3A particles. This was said to result in reduction of the number of dissolution sites which would otherwise be available for the hydroxide ions to catalyze the dissolution.

Collepari et al. [15] did not confirm the idea that retardation of C_3A hydration occurs as results of SO_4^{2-} ion absorption, by showing that Na_2SO_4 did not retard C_3A hydration.

Though the results reported in the literature are contradictory in many cases, the conditions of the experiment were different from each other and different from those of the real cement systems. Some of the experiments were carried out in diluted suspensions, although others were closer to the real conditions of cement use.

Locher et al. [16] extensively investigated the mechanism of set of cement paste and the role of calcium sulfate in it. They considered that recrystallization of ettringite played a major part in setting. A thin ettringite layer was said to form rapidly on the surface of cement particles but did not reduce the workability of the paste.

Recrystallization of this microcrystalline ettringite into large needlelike crystals was then said to bridge the spaces between adjacent particles and cause setting. Locher et al. also considered that the reactivity of the specific C_3A present modifies the formation of ettringite, and consequently the setting time. Formation of the thin layer of ettringite and recrystallization of ettringite were accelerated when C_3A is highly reactive.

In contrast, Jawed et al. [11] had a different view on set, and considered that it depended primarily on the alite hydration rather than on ettringite formation. The beginning of the second heat evolution peaks was generally considered as the start of the rapid period of calcium silicate hydration, and the resulting rapid C-S-H formation was said to coincide with the initial set. Microscopic investigations on the solid phase, for example by Scrivener [17] also supported the idea that the set was caused by accelerated formation of CSH (and CH), rather than by the secondary growth of ettringite crystals.

Uchikawa et al. [18] considered that the set mechanism was related to both ettringite formation and alite hydration. They stated that differences in the amount and the morphology of ettringite formed resulted in different set times, especially for the case of well burnt clinker. For poorly burnt clinker however, vigorous hydration of alite and formation of C-S-H gel contributed more to the setting time.

Uchikawa et al. [18] also measured the concentration of the Ca^{2+} and OH^- and SO_4^{2-} ion in suspension (water:cement ratio = 4.0) of clinker with three different

forms of the CaSO_4 , i.e., gypsum, hemihydrate, and insoluble anhydrite. Influences of the form of CaSO_4 were observed on the concentration of the Ca^{2+} ion and the SO_4^{2-} ion, but not on that of the OH^- ion. The CaSO_4 saturation ratio observed increased in the order of anhydrite, gypsum, and hemihydrate added to clinker. When hemihydrate was used, there was a sudden decrease in the CaSO_4 saturation ratio due to the secondary gypsum formation.

Odler et al. [19] examined the effects of the different forms of the calcium sulfate and found that the rate of ettringite formation was reduced and the beginning of its conversion to the monosulfate was delayed if anhydrite was used as the CaSO_4 , compared to the hemihydrate or gypsum.

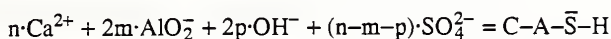
Tang and Gartner [20] showed that the chemical and physical form of the calcium sulfates as well as the amount added were very important factors in governing the characteristics of early cement paste hydration. They examined mixtures of a clinker and a various sources of the sulfate ion, including calcium sulfates as gypsum, hemihydrate, and insoluble anhydrite; alkali calcium sulfates as calcium langbeinite ($2\text{CaSO}_4 \cdot \text{K}_2\text{SO}_4$) and syngenite ($\text{CaSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot \text{H}_2\text{O}$); and alkali sulfates as aphthitalite ($3\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$). The presence of relatively soluble sulfates retarded the initial C_3A hydration (for the first 2 minutes) and the rate at which C_3A was dissolved and converted to ettringite varied significantly with the form of the sulfate added. They also found that increasing physical distribution of gypsum by intergrinding resulted in a smaller initial extent of C_3A hydration.

These authors summerized a mechanism of sulfate phase reactions in a series of chemical reactions of different velocities as follows:

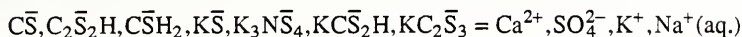
1. Initial dissolution of the calcium aluminate (rapid, very exothermic)



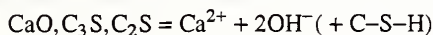
2. Formation of initial protective hydrate layer (rapid)



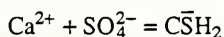
3. Initial dissolution of sulfate phases (at various rates)



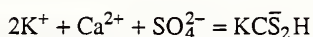
4. Initial dissolution of CaO and calcium silicates (at various rates)



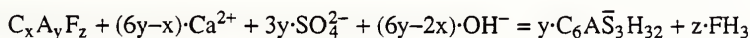
5. Establishment of gypsum equilibrium (fairly rapid)



6. Establishment of syngenite equilibrium (fairly rapid)



7. Steady consumption of CaSO₄ to form ettringite (slow)



Tang and Gartner considered that the step 2 reaction is formation of protective layer onto the calcium aluminate surface which retards the calcium aluminate dissolution (step 1) and this layer may well be amorphous. The step 7 reaction is a slow pre-

precipitation of ettringite which is probably limited by diffusion of one of the components through the protective layer. After the step 7, when the sulfate supply is almost completely exhausted, that is, the sulfate near the calcium aluminate surface becomes insufficient to continue the reaction in the step 7, the ettringite layer becomes unstable and decomposes into the AFm phase.

Tang et al. [20] also considered that the secondary gypsum or syngenite formation from hemihydrate or calcium langbeinite, respectively, reduced the fluidity of the paste, or caused "mild false set". Locher [16] observed the same phenomena.

Penko [21] tested a low alkali content clinker with addition of gypsum or alkali sulfate or both, and found that the dissolution rate of gypsum controlled the rate of formation of ettringite and the time of the conversion from the SO_4^{2-} ion to the OH^- ion in the liquid phase. If alkali and gypsum were overdosed in the cement system, gypsum remained undissolved longer and thus the SO_4^{2-} ion concentration did not drop within a day.

Penko concluded that the undissolved solid gypsum in the cement system is the source of the slowly dissolving SO_4^{2-} ion, and the limitation on its conversion to ettringite. The alkali sulfate on the other hand, dissolved quickly in the liquid system, provided the SO_4^{2-} ion needed for initial ettringite formation, and caused the alkalinity resulted from hydrolysis.

2.2 Performance of Superplasticizers

An overview of research on cement paste with superplasticizer is provided in this section, which incorporates certain features in the hydration of cement free of admixture.

2.2.1 Mechanism of Superplasticizer Adsorption

There are a number of variations in the superplasticizers with regard to their chemical structure, but the two widely used have as their main component either naphthalene sulfonate or melamine sulfonate. Purified lignosulfonates are also used as superplasticizers, but to a lesser degree.

Naphthalene sulfonate based superplasticizers were developed in Japan, and the pioneering research work was summarized in a paper by Hattori [22]. Melamine sulfonate superplasticizer was developed in Germany [23]. The molecular structure of these superplasticizers are shown in Fig. 3.2-1. Both polymer structures are of reasonably long chains on which electric charge donor groups such as $-\text{SO}_3^- \text{M}^+$ are attached.

The actions of the two types of superplasticizer are basically the same. Generally speaking, the superplasticizer chains are adsorbed on the cement particles and thereby introduce strong negative charges on the particles at their interfaces with the solution; this results in an electrostatic repulsion between particles. This causes the dispersion of particles and reduces the viscosity of the cement paste. However, this view is too

general, and it will be discussed further.

The zeta potential of the cement particles is a key parameter to understand the performance of the superplasticizer, since the electrostatic force between particles is considered to be the essential driving force for the adsorption of the superplasticizer and for the fluidification of the paste.

Tattersall and Banfill [24] explained that the cement particles can obtain a charge either as a result of imperfections in the crystal structure near the surface (disorders), or through the preferential adsorption of specific ions on the surface.

When the superplasticizer is pre-dissolved in the mix water, the hydration of the cement grain and the adsorption of the superplasticizer onto the cement particles take place simultaneously in the first few minutes after the contact. However it is difficult to differentiate, in real cement hydration, whether the adsorption is on the anhydrous cement particles or on their early hydration products.

Nawa et al. [25] cited the work of Mascolo and Marroccoli [26], who investigated the reactivity of calcium aluminate hydrates. Based on the idea that the structure of $C_4A \cdot nH$ is a complex salt that consists of positively-charged $[Ca_2Al(OH)_6]^+$ balanced by negatively-charged interlayers of composition $[OH^- \cdot mH_2O]$, they concluded that the interlayer OH^- anion of the $C_4A \cdot nH$ could be easily exchanged with various anions, and that its selectivity of anions in exchanging were determined primarily by the valence of the anion. Then Nawa et al. [25] suggested that the sulfate ion or the sulfonate group of the superplasticizers could be exchanged with the OH^- ion in the

calcium aluminate hydrate phases. This was suggested as another interpretation of the adsorption phenomena.

2.2.2 Mechanism of Cement Particle Dispersion

According to Tattersall and Banfill [24], the concepts of interparticle forces, based on the Derjugin-Landau-Verwey-Overbeek (DLVO) theory would be explained as follows. The electric double layer consists of a layer of charged particle surface and counterions electrostatically attracted to the surface but exponentially diffuse away toward the bulk solution. When two particles approach each other in a suspension, their diffuse double layers begin to repel each other. Simultaneously, there is a force of attraction between particles due to van der Waals forces, which decreases with distance of the particles. By adding these repulsion and attraction, it is found that the resultant potential energy curve for particle interaction has a minimum value at a distance where an equilibrium is achieved. As the electrolyte concentration increases, the electrical double layer is compressed and the energy barrier decreases to nothing so that colliding particles can fall into the every minimum and stick together, and thus flocculate.

However, there are criticisms for treating flocculation in cement paste by the usual DLVO equations of colloid chemistry. Diamond [27] presented several reasons, including the large size of most of the ground clinker particles, the multitude of chemical phases that are exposed on the cement particle surfaces, the high volume concentration of the particles in paste of normal water:cement ratio, and the fact that

chemical reactions are occurring on the surface even during the dormant period.

Tattersall and Banfill [24] described that the condition of a cement-water suspension can be modified in three ways that will prevent the formation of a flocculated structure as follows.

- i. Expansion or contraction of the electrical double layer around the particles.
- ii. Generation of electrical repulsive forces between particles by adsorption of ionized compounds.
- iii. Build-up of protective steric barriers to flocculation.

They considered that the mechanism of deflocculation induced by the superplasticizers was a mixture of both effects ii. and iii. listed above.

The steric effect is such that when adsorbed molecules form multilayer structure around the particle, the particles cannot physically approach each other so closely as the equilibrium potential distance. This skin of adsorbed molecules is also called a steric barrier. Taylor [6] considered that this steric effect is not a major action induced by superplasticizer. He considered the evidence convincing that uptake was mainly by the hydration products, and that significant amounts of the superplasticizer were absorbed as well as adsorbed. He supported the idea of an increase in zeta potential being the primary force.

Daimon et al. [28] added another possible mechanism of decreasing flocculation, which was an increase in solid-liquid affinity, but they considered the contribution of

this mechanism to be small.

The state of the superplasticizers adsorbed at the interface are usually modeled as long chains consisting of polymer mingled and attached loosely on the surface at relatively small numbers of negative sites [29]. Kondo et al. [30] acknowledged this adsorbed state as "loop" adsorption in contrast to "train" adsorption, in which the adsorbed polymer is stuck closely to the adsorbent. In "loop" adsorbed state, most of the active negative sites on the chains are in the neighborhood of the particle, but not neutralized by the charge on the cement surface. Andersen [31] considered that this gives more negative charges or the zeta potential onto the particle, which could also compress the electric double layer.

The fluidizing effect of the superplasticizer depends on its molecular weight. It has been generally considered that the higher the molecular weight, the more fluidity is imparted to the paste [15]. However, Hattori [22] stated that maximum superplasticizer performance was obtained for naphthalene sulfonate polymers with a degree of polymerization of about 10.

Andersen et al. [32] investigated the effect of the molecular weight of sulfonated polystyrene superplasticizer, and found that the optimum molecular weight to give the maximum adsorption onto an ordinary portland cement was 16,000 g/mole; superplasticizers of larger molecular weights were less adsorbed onto the cement, but gave a larger negative zeta potentials.

Experimental techniques usually used in investigating the effect of degree of polymerization include gel permeation chromatography (GPC) to determine the molecular weight distribution of the polymer, and an ultrafiltration process (UF) to remove the low molecular weight fraction [33, 34].

2.2.3 Absorption Characteristics

The adsorption of the superplasticizer at the first stage of hydration has been considered as the adsorption of organic molecules onto the solid. This topic has been investigated from the interest of the mechanism of organic retarders which are usually smaller molecules. In 1972, Young [35] carried out an extensive review on the mechanism of retardation. He stated that the admixtures in general were preferentially adsorbed onto the aluminate phases in the very early stage of the cement hydration, and were largely removed from the liquid phase.

The adsorption of salicylic acid was investigated by Blank et al. [36], and their results showed that the amount of adsorption onto the different cement minerals were in the order of $C_3A > C_4AF \gg C_3S$, but adsorption were measured in organic solution.

Diamond [37-39] studied the suspension of C_3A and C_4AF in the solution of salicylic acid. He observed a precipitation of a largely amorphous hydration product containing significant amount of salicylate, and considered that this phase is mainly due to removal of the salicylic acid from solution. Then he suggested that the interaction

between aluminum-bearing cement and hydrating cement compounds and salicylic acid is different from the simple physical adsorption.

As with other organic compounds, it is known that the amount of the superplasticizer adsorbed on different cement minerals are different. Adsorption onto pure C_3A and C_4AF are much larger than onto pure C_3S and C_2S , and are larger than overall adsorption onto ordinary portland cement [40, 41].

But again, there is a complication in that the adsorption onto the anhydrous or hydrated phases are not differentiated by adsorption experiments in an aqueous suspension. Massazza et al. [42, 43] examined the suspension of C_3A , ettringite, monosulfate in a non-aqueous solution of dimethylsulphoxide (DMSO) and obtained adsorption isotherms of superplasticizers showing considerable adsorption on calcium sulfoaluminate phases but little adsorption on C_3A .

Ramachandran [44] also obtained the similar results by examining C_3A -gypsum- H_2O system with superplasticizers. In addition, he diluted the aqueous suspension and did not detected any desorption of superplasticizer (naphthalene sulfonate and melamine sulfonate) which adsorbed on the surface of hydrated aluminate or sulfoaluminate phases. Taylor [6] cited several works which studied the anhydrous and hydrated compounds in aqueous and non-aqueous media and quoted that calcium lignosulphonate and superplasticizers were adsorbed by CSH, AFm phases or CH but not by C_3S , C_3A , or C_3AH_6 .

Suzue et al. [40] compared the adsorbed amount of the superplasticizer in the suspension of each cement mineral separately for the cases with and without the presence of gypsum. Where there was no gypsum, the adsorption onto C_3A and C_4AF was about ten times as much as with gypsum present. They also showed that the adsorption of superplasticizer pre-dissolved in the mix water onto C_3A and C_4AF was significantly higher than that when the superplasticizer was added after the contact with water, which tends to explain the advantage of the late addition of the superplasticizer.

Chiocchio et al. [45] claimed that the optimum time to add the superplasticizer was at the beginning of the induction period. They remarked that a large portion of admixture added before the intense first C_3A hydration period was over, was taken up by the early hydration product of the aluminate phase and immediately covered by the subsequent hydration product. Thus the dispersing action was inefficient.

Andersen et al. [46] found that the average negative zeta potential of cement particles in the presence of naphthalene sulfonate superplasticizer decreased with increasing degree of $CaSO_4$ saturation. They attributed this to the compression of the electric double layer in a stronger ionic solution which also caused the less adsorption of the superplasticizer.

The effects of the alkali sulfate in cement is also important to the adsorption behavior. Nawa et al. [47] found that the adsorption of the naphthalene sulfonate superplasticizer on C_3A was greatly reduced in the presence of Na_2SO_4 . The pres-

ence of the sulfate ion derived from either calcium sulfate or alkali sulfate decreased the adsorption of naphthalene sulfonate on C_3A and C_4AF , but increased the adsorption on C_3S .

In order to investigate this compositional difference in adsorption characteristics, attempts were made by many researchers to determine the zeta potential of each cement mineral separately. Tadros et al. [14] showed that the zeta potential of C_3A was initially positive, but it went down to zero due to the adsorption of the sulfate ions derived from either hemihydrate or K_2SO_4 . Zelwer [48] concluded that the zeta potential of C_3S and of cement particles were negative in the absence of admixtures. That of C_3A particle was reported to be positive. Nawa et al. [25] also confirmed that in pure water, the zeta potential of C_3A and C_4AF was positive, whereas it was negative for C_3S . In addition, the zeta potential of C_3A and C_4AF changed from positive to negative when either the sulfate ion or naphthalene sulfonate superplasticizer were added to the suspension.

Thus they concluded that fresh cement paste suspension consists of particles having different values of zeta potential, and that since the naphthalene sulfonate and the sulfate ion are both negative they tend to be adsorbed competitively on the C_3A or C_4AF surfaces which initially have positive zeta potentials.

2.2.4 Effects of Superplasticizer on Early Hydration

The addition of superplasticizer to cements results in a more dispersed state of the cement particles. This exposes a larger surface area, and thus the cement hydration is promoted. However, the addition of the superplasticizer also leads to retardation by an inherent mechanism, in which the adsorbed long chain polymer coats the surface of the cement particles and hinders further hydration.

Odler and Becker [49] found that the hydration of C_3S was retarded by all three types of superplasticizers (naphthalene sulfonate, melamine sulfonate, and lignosulfonate).

Massazza et al. [42, 43] investigated effects of the superplasticizer on C_3A hydration. He found that both naphthalene sulfonate and lignosulfonate slowed down the rate of ettringite formation. He also noticed a damage of morphology of the ettringite associated with the incorporation of superplasticizer, in that the size of the ettringite was smaller with the admixture.

Ramachandran [44] found in a suspension of C_3A -gypsum- H_2O that the rate of hydration at very early age to form ettringite was accelerated by the superplasticizers (naphthalene sulfonate and melamine sulfonate), but conversion to monosulfate, corresponding to the second heat evolution, was retarded.

Aitcin et al. [50] classified cement particles into three fractions by size i.e. coarse, medium, and fine, and compared the degree of retardation caused by the naphthalene based superplasticizer on each fraction. The medium fraction ($30\mu m$ -

4 μm) was the most retarded, whereas the fine fraction ($< 4\mu\text{m}$) showed almost no retardation. Chemical analysis showed an increase in SO_3 and alkali contents in the finer fraction compared to the others.

Nawa et al. [47] showed that the retardation effect of naphthalene sulfonate superplasticizer increased with increasing alkali sulfate content of the cement. They suggested that the alkali sulfate hindered the adsorption of the admixture onto the aluminate phases, permitting larger adsorption on the silicate phases such as C_3S and C_2S , which delayed the overall hydration.

The calcium salt of naphthalene sulfonate superplasticizer has been generally considered as non-retarding. However, whether the hydration was retarded or not by the calcium salt depended on the chemical composition of the cement, as shown for example by Basile et al. [51].

2.2.5 Effects of Superplasticizer on Rheological Characteristics

The rheology of the cement paste has been investigated for long time but general agreement has not been reached, probably because the experimental results were highly dependent upon the experimental methods used including the apparatus and the mixing procedure. In this section, the review is limited to those papers which examined the effect of superplasticizer on rheological properties.

Banfill [52] cited the work by Petrie [53] who found that, as the dosage of a naphthalene based plasticizer increased, the flow behavior changed from Bingham to reversible Newtonian, i.e. the width of the hysteresis loop and the yield value decreased. A similar result was found by Banfill [54], in that a naphthalene sulfonate reduced both the yield value and the hysteresis loop area almost to zero.

Daimon and Roy [28, 55] carried out an extensive study on the rheology of the paste relating with the adsorption characteristics of superplasticizers and the zeta potential generated thereby in the suspension. They found that the zeta potential obtained was proportional to the amount of superplasticizer adsorbed, and to the fluidity of the paste, and concluded that zeta potential was the cause of improved dispersion.

Banfill [52] studied the effect of both naphthalene sulfonate and melamine sulfonate superplasticizers on the flow properties of a cement paste of 0.35 water:cement ratio. The yield value of the cement paste decreased virtually to zero at high dosage, whereas the plastic viscosity decreased about 40% to a minimum value and then increased slightly with further increase in the concentration of the admixture. He also stated that both yield value and plastic viscosity of the paste were affected more by the melamine sulfonate than by the naphthalene sulfonate at equal dosage.

Not much work has been reported with regard to the mechanism through which the adsorption causes an improvement in the workability of the paste. Massazza et al. [56] examined suspensions of C_4AH_{13} and C_3AH_6 in lime water with superplasticiz-

ers, and reported poor correlation between the zeta potential value of calcium aluminate hydrates in those suspension and the apparent viscosity of the paste.

Researcher such as Ramachandran [44] considered that the viscosity of the paste depends on the amount superplasticizer adsorbed on the silicate phases. Suzue et al. [40] reasoned that the effectiveness in increasing fluidity of late addition of the superplasticizer is due to a larger adsorption on the silicate phases. With early addition some superplasticizer is removed from the liquid almost immediately by the rapidly hydrating aluminate phase. Nawa et al. [47] measured zeta potentials of calcium silicate particles and of calcium aluminate particles in superplasticized cement systems, and found that both kinds of particles, were charged negatively. However, they found that the aluminate particles had a higher absolute potential than the silicate particles. They suggested that this reflects greater uptake of the superplasticizer by the aluminate particles. Since the viscosity of the suspension is governed mainly by the repulsion between silicate particles, this effect was considered to result in larger viscosity than would have been produced by the superplasticizer of aluminate particles had not been present.

The form of the calcium sulfate present in a given cement has several effects on the rheology of superplasticized cement paste. The rate of the dissolution of free calcium sulfate is generally considered to decrease in the series, hemihydrate > gypsum >> anhydrite. Basile et al. [51] tested the effect of the CaSO_4 form on the rheology of cement paste using the mini slump cone. Two clinkers, each with either gypsum or hemihydrate were examined with and without the addition of naphthalene sulfonate

(calcium salt) superplasticizer. The fluidity of the superplasticized paste was always higher with gypsum than with hemihydrate.

The same result was obtained by Nawa et al. [47]. They compared the effects of the three form of calcium sulfate (gypsum, hemihydrate, anhydrite) on the viscosity of superplasticized cement paste as measured by a coaxial cylinder viscometer. They found that pastes with low alkali clinker and anhydrite always showed extremely high viscosity regardless of the dosage of the superplasticizer. For a medium and a high alkali clinker, the viscosity of the paste was found to decrease in the order of hemihydrate, anhydrite, and gypsum.

2.2.6 Superplasticized Concrete

The rheological behaviors of superplasticized concrete has been associated with the characteristics of the pastes discussed so far. Rixom and Waddicor [57] measured the rheological parameters of a superplasticized concrete as a function of the dosage of the admixture, by using special apparatus capable of measuring the torque when mixing. They found that the yield value was significantly reduced by the admixture but the plastic viscosity was not much reduced. Tattersall and Banfill [24] reached the same conclusion.

Slump loss is one of the major problems for concrete with superplasticizer. The stiffening rate depends greatly on the specific cement composition, especially the relative proportions of sulfate and C_3A . Meyer and Perenchio [58] stated that the rate of

slump loss increased as C_3A content of the cement increased, and Khalil and Ward [59] stated that the rate of slump loss decreased with increasing SO_3 content. Basile et al. [51] stated that the rate of slump loss of concrete with superplasticizer appeared to be higher in concrete with cement containing hemihydrate than with cement containing gypsum.

2.2.7 Admixture - Cement Incompatibility Problems

A few cases of admixture-cement incompatibility problems are described for reference. It is well known that lignosulfonate admixture sometimes causes abnormal quick setting. Some work such as that of Coulon [60] suggested that the sulfate and C_3A contents were important in this regard. He concluded that lignosulfonate admixture inhibited the dissolution of sulfate from the cement for a limited time so that free hydration of C_3A could take place, giving flash set. Dodson et al. [61] tested the effects of different forms of calcium sulfates and reported that natural anhydrite with portland cement clinker could produce flash set in paste in presence of calcium lignosulfonate admixture. The rate of dissolution of natural anhydrite in lime water is slower than those of gypsum or hemihydrate, as other researchers have pointed out [16, 62, 63], but in addition, Dodson et al. showed that the dissolution rate of natural anhydrite was significantly reduced where lignosulfonate admixture was present. They considered that this was probably caused by the adsorption of lignosulfonate onto natural anhydrite particles, which retarded their dissolution.

Other instances of admixture-cement incompatibility involve the results of delayed conversion of hemihydrate to gypsum. When this process, normally completed during the mixing cycle, is delayed, false set may be exhibited. Adsorption of lignosulfonate (or other organic admixtures) onto hemihydrate surfaces may, in a few cases, delay its conversion to gypsum and so induce tendencies toward the occurrence of false setting.

Tattersall [24] reported a particular case that the yield value measured for concrete was about 3 times as high when a calcium lignosulfonate admixture was used. This kind of difficulty could be overcome by late addition of the lignosulfonate after a few minutes' mixing.

This importance of the mixing sequence was early discussed for the set-retarding admixture by Bruere [64], who found that about several minutes late addition of lignosulfonate had remarkably extended the induction period compared to the case where admixture was predissolved.

Grutzeck [65] reported a case of potential incompatibility between salt and superplasticizer. Mixing of saturated NaCl solution with the naphthalene sulfonate superplasticizer caused extreme foaming.

CHAPTER THREE

MATERIALS

3.1 Cement

Two different kinds of ASTM Type I ordinary portland cement and one white cement were used for the study. The mill analysis of each cement was provided by the cement manufacturers, and is shown in Table 3.1-1. In addition, the SO_3 content determined in this laboratory by the author is also shown in the table. The physical data of each cement provided by the cement manufacturers is shown in Table 3.1-2.

The first cement, designated cement "L", was produced by Lone Star Industries at Greencastle, IN. This particular cement has been used in the Materials Area Concrete Laboratory at Purdue University as a standard laboratory cement (Laboratory No. 326), and considered to be representative of cements in northern and central Indiana.

The second cement, designated cement "S", was produced by Southwestern Portland Cement Co. in Fairborn, OH. This particular cement has also been used in prior studies at Purdue University, and is considered as representative of cements used in southern Indiana.

The white cement "W" is a sulfate resisting ASTM Type I portland cement, produced by Aalborg Portland A/S, Denmark, and supplied through the Lehigh Portland

Table 3.1-1 Mill analysis and Bogue composition of cements

Chemical Analysis (%)			
Type of Cement	Cement "L"	Cement "S"	Cement "W"
SiO ₂	20.98	20.6	23.88
Al ₂ O ₃	5.38	4.0	1.94
Fe ₂ O ₃	2.46	3.1	0.42
CaO	64.34	61.36	70.03
MgO	1.09	4.9	-
SO ₃	3.03	2.8	1.82
Na ₂ O	0.09	0.25	0.10
K ₂ O	0.72	0.90	0.02
Alkalis, Na ₂ O equiv.	0.56	0.85	0.083
Loss on Ignition	1.40	1.9	1.50
Insoluble Residue	0.23	0.28	
SO ₃ (analyzed by author)	3.17	-	3.13
Bogue Composition (%)			
C ₃ S	54.14	54.0	74.2
C ₂ S	19.39	18.36	12.5
C ₃ A	10.10	5.35	4.4
C ₄ AF	7.47	9.43	1.3
CaSO ₄	5.15	4.76	3.1

Table 3.1-2 Physical data of cements

Physical Data			
Type of Cement	Cement "L"	Cement "S"	Cement "W"
Blaine Fineness (cm ² /g):	3275	3720	-
Fineness (#325, % passing):	83.7	-	-
Soundness:			
Autoclave Expansion (%):	0.011	0.18	-
Normal Consistency: (%)	25.0	-	-
Time of Setting:			
Gillmore Initial (hr:min)	1:55	-	-
Gillmore Final (hr:min)	3:50	-	-
Vicat Initial (hr:min)	1:25	2:27	-
Vicat Final (hr:min)	3:00	4:00	-
Air Entrainment (% by volume):	9.7	7.6	-
Compressive Strength (psi): (2 inch Mortar cubes)			
1-Day	2140	1780	-
3-Days	3430	3090	-
7-Days	4290	4190	-
28-Days	5380	5360	-

Cement Co., Allentown, PA.

X-ray diffraction patterns of those three cements are provided in Fig. 3.1-1 to Fig. 3.1-3.

Cement L has a relatively high C_3A content. It has 5.15% of $CaSO_4$ according to the Bogue calculation, and the mineral form of the $CaSO_4$ is hemihydrate.

Cement S contains an unusually high MgO content, 4.9%. The alkali content is 0.85% Na_2O equivalent, somewhat higher than that for cement L. The form of $CaSO_4$ is a mixture of hemihydrate and gypsum.

The white cement was selected for use in this study because of its very low alkali content (0.083% Na_2O equivalent). It also has low contents of both aluminum and iron. The SO_3 content by the author's analysis is in the normal range, 3.13%, in contrast to the mill analysis data, which indicated only 1.82%. The XRD pattern shows that the calcium sulfate is completely in the form of natural anhydrite (insoluble anhydrite), and DSC analysis does not show any dehydration peak.

3.2 Superplasticizer

The two most popular superplasticizer types, based respectively on naphthalene sulfonate and melamine sulfonate were studied in this research. The molecular structure of the repeating unit of each of these polymeric types is shown in Fig. 3.2-1.

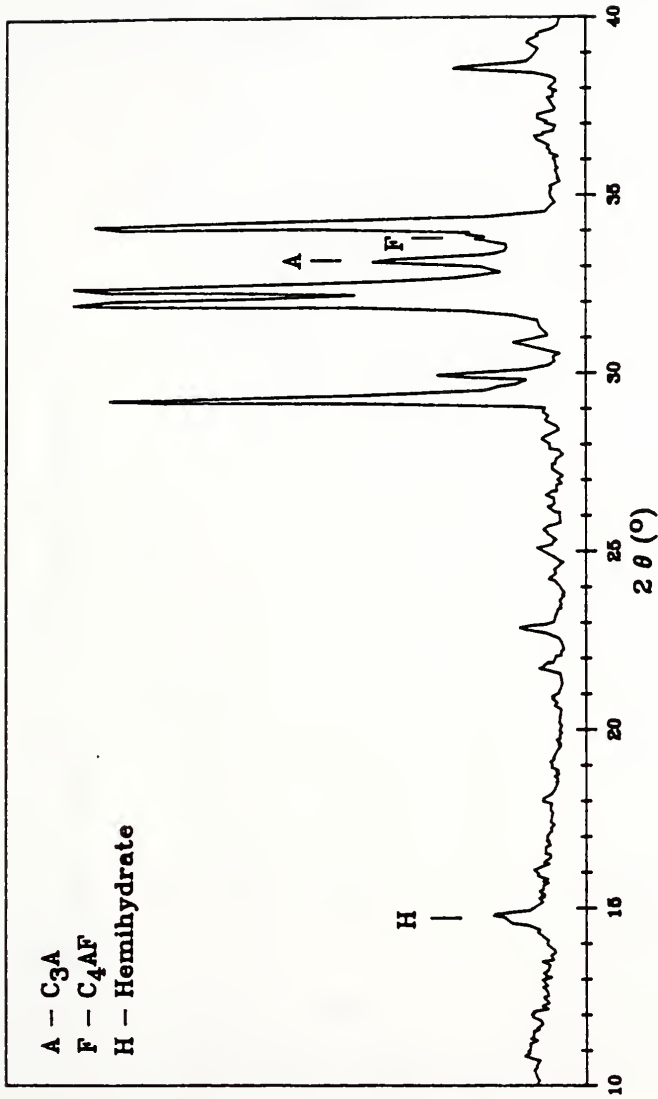


Fig. 3.1-1 X-ray diffraction pattern for cement "L"

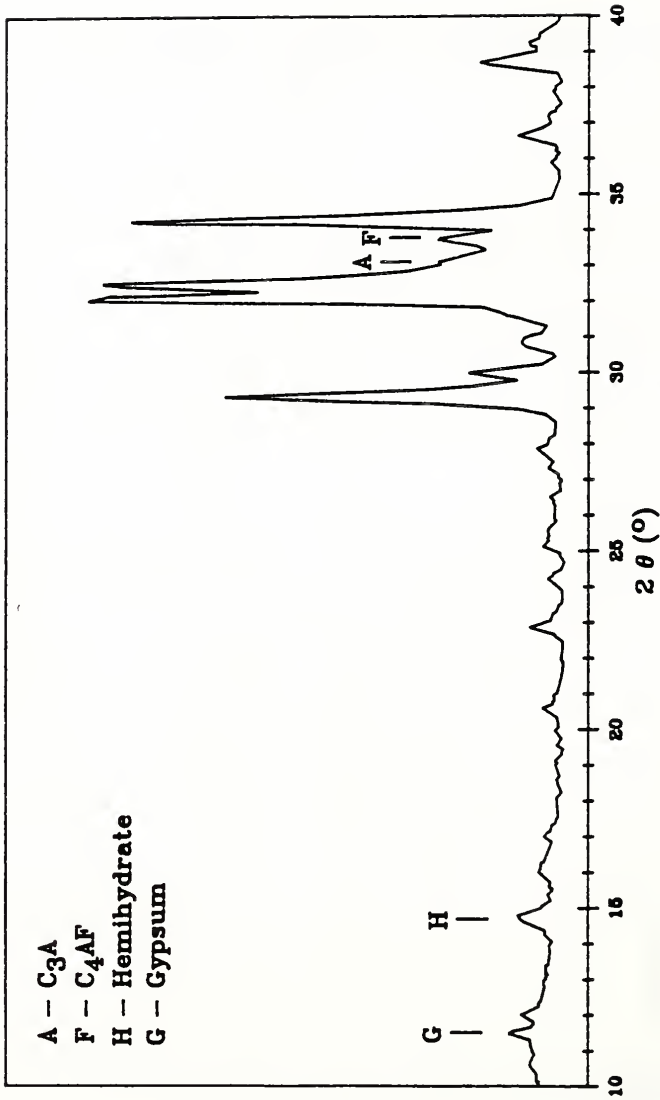


Fig. 3.1-2 X-ray diffraction pattern for cement "S"

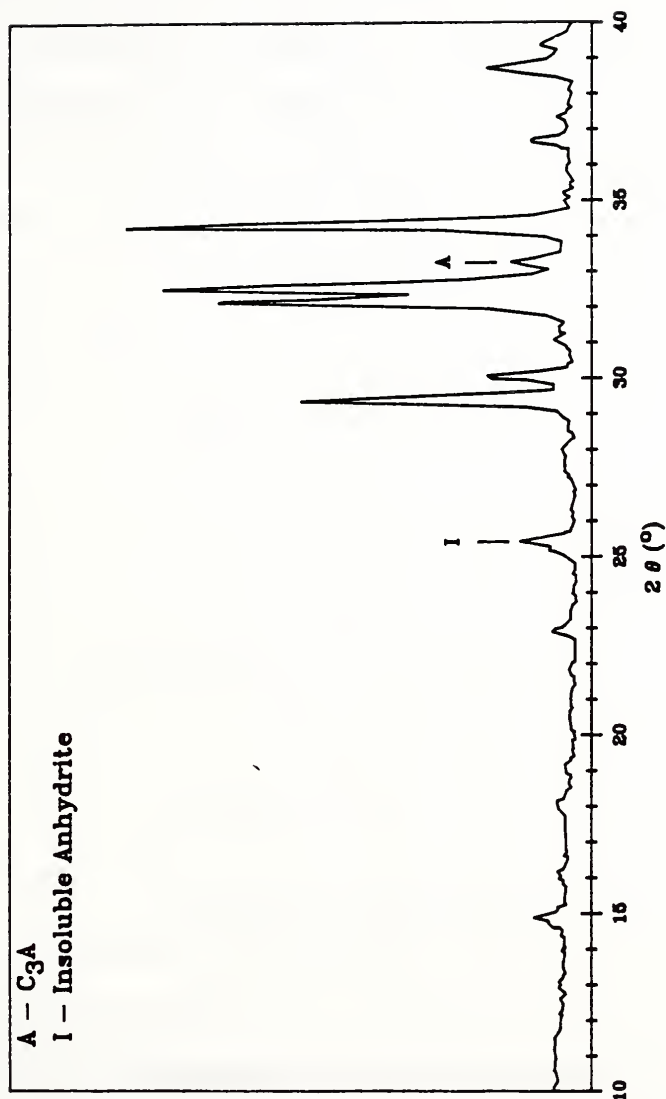
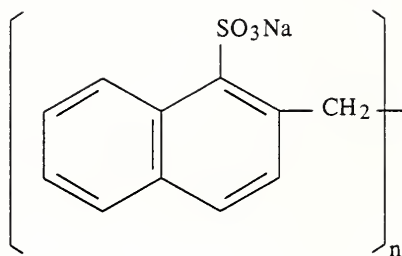
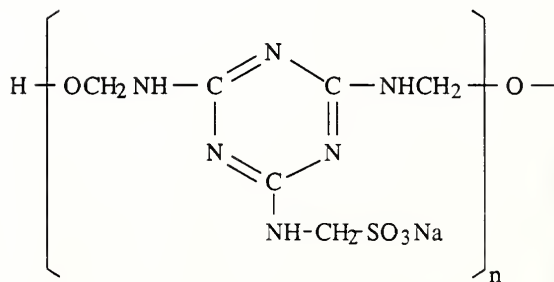


Fig. 3.1-3 X-ray diffraction pattern for white cement "W"



Naphthalene Sulfonate Superplasticizer



Melamine Sulfonate Superplasticizer

Fig. 3.2-1 Molecular structure of superplasticizers

3.2.1 Naphthalene Sulfonate Superplasticizers

Two commercial superplasticizers, classified into the category of sodium beta-naphthalene sulfonate formaldehyde condensate, were used in this adsorption study. The first superplasticizer, designated superplasticizer "A", was supplied by the W.R. Grace Co.. It is a dry solid product and was used in the study reported by Burk et al. [66] of W.R. Grace Co. (their designation "Admixture A1"). The second superplasticizer, designated superplasticizer "B", was a commercially-available solution form of "Mighty 150", produced by Kao Corporation.

Both superplasticizers are not simple materials, but mixtures of monomers, polymeric species of various degree of polymerization (chain lengths), and some inorganic salt impurities. In Table 3.2-1, chemical analysis data and physical properties of superplasticizers are summarized. A breakdown of the molecular species present in superplasticizer A was obtained from the paper by Burk et al. There are no similar data available for superplasticizer B or the melamine sulfonate superplasticizer.

The solid content of the superplasticizer B was determined by drying the sample of known volume in oven at 105°C, and it was found to be 52%.

To determine the inorganic components quantitatively, the original mixing water containing the specified amount of pre-dissolved admixtures was chemically analyzed. The contents of each element in the original admixture were calculated, and are also shown in Table 3.2-1. The inorganic salt impurity contents of each admixture were calculated from the contents of SO_4 in solution, assuming that the SO_4 in the original

Table 3.2-1 Chemical and physical data on superplasticizers

Chemical Analysis Data (%)			
	Naphthalene Sulfonate		Melamine Sulfonate
Superplasticizer	A	B	M
Solid Components (%):			
Monomer	8.18	-	-
Nonadsorbables (mostly dimer & trimer)	10.49	-	-
Higher Polymers	68.03	-	-
Na ₂ SO ₄	13.3	-	-
Inorganic composition (by analysis) (%):			
Na	11.6	8.6	9.5
K	0.0	0.1	0.2
Ca	0.2	0.7	0.1
OH	-	-	1.6
SO ₄	3.2	0.7	2.5
NaOH estimated	-	-	3.7
Na ₂ SO ₄ estimated	4.7	1.0	3.7
organics composition (by subtraction) (%):	85.0	89.9	86.1
organics charge density (meq/g):	5.26	4.45	3.24
Physical Properties			
Solid content (kg/L):	solid	0.518	0.333

admixture was derived from Na_2SO_4 impurity. Then the organic fraction of each admixture was estimated by subtraction of all inorganic elements.

For superplasticizer A, the Na_2SO_4 content is calculated as 4.7 %, which is much less than 13.3% obtained by Burk et al. However, the organics content of 85.0 %, estimated by subtraction is similar to the sum of the monomer, nonadsorbable, and higher weight polymers reported in Burk et al.'s data. These percentages do not include the alkali ions associated with the polymer. The apparent inorganic impurity level in superplasticizer B was somewhat less than that of superplasticizer A, the estimated Na_2SO_4 content being only about 1%. The organic content of the solids (less the associated alkali contents) was 89% as compared to 85% in superplasticizer A. This compositional comparison of the two superplasticizers will be discussed further in Chapter 5.

3.2.2 Melamine Sulfonate Superplasticizer

The melamine sulfonate superplasticizer used was a commercial products, Melment, obtained from Gifford Hill Co.. The admixture was supplied as a solution, and no molecular composition data was available. The solids content was 33%, and the results of chemical analyses are also shown in Table 3.2-1.

A considerable content of sodium found by the chemical analysis, is mostly the counter cation to the negatively charged sulfonic acid site of the polymer. Though the sulfate ion was the largest anion impurity, a significant amount of OH ion was

detected in the original admixture solution, whereas other naphthalene sulfonate admixtures were conditioned almost neutral or slightly acidic.

CHAPTER FOUR

EXPERIMENTAL WORK AND METHODS USED

4.1 Summary of Mixes and Analyses

Table 4.1-1 summarizes the cement paste mixes designed in this study and the elemental analyses done for each mix. The mix code is defined such that the first capital letter refers to the kind of cement, the second capital letter refers to the kind of superplasticizer, and the third and fourth letters refer to either the kind of alkali sulfates added or the dosage of the added alkali hydroxide where used.

The first capital letter is either W, L, or S, which signifies that the paste is of the white cement W, the ordinary portland cement L, or the other ordinary portland cement S, respectively.

The second capital letter is either A, B, or M, which is designated as naphthalene sulfonate superplasticizer A, or naphthalene sulfonate superplasticizer B, or melamine sulfonate superplasticizer M, respectively. The capital letter O means a control paste without any superplasticizer.

The third letter is either a number 0 thru 5, or a capital letter K, or N. When KOH is added to the mix water, a number is used to signify the level of dosage. (0 means no addition of KOH.) The letter K or N means that either K_2SO_4 or Na_2SO_4 is added to

Table 4.1-1 Summary of mixes and analyses

Mix code	WO	WA0	WA1	WA2	WA3	WA4	WA5	WB0	WB10	WB3	WB3'	WB3	WBK	WBN	LO	LB	LM	SO	SB	SM
Concrete	W	W	W	W	W	W	W	W	W	W	W	W	W	W	L	L	L	S	S	S
Superplasticizer	-	A	A	A	A	A	A	B	B	B	B	B	B	B	-	B	M	-	B	M
Dosage, %	-	2.0	2.0	2.0	2.0	2.0	2.0	1.55	1.55	1.55	1.55	1.55	1.55	1.55	-	1.55	0.5	-	1.55	1.55
Added alkali	-	-	KOH	KOH	KOH	KOH	KOH	-	N5	KOH	KOH	K5	N5	-	-	-	-	-	-	-
Dosage, %	-	-	0.3	0.45	0.6	0.9	1.2	-	0.03	0.6	0.6	1.2	0.6	0.6	-	-	-	-	-	-
Sampling time																				
prior to cast	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
set to 1 day	X	-	-	-	-	-	-	X	-	-	-	-	-	-	X	X	X	X	X	X
3, 7, 14 days	X	-	-	-	-	-	-	X	-	-	-	-	-	-	-	X	X	X	X	X
Solution phase analysis																				
Superplasticizer by	-	X	X	X	X	X	X	X	X	X	X	X	X	X	-	X	X	-	X	X
UV spectroscopy																				
R ⁺ , Na ⁺ , Ca ²⁺	X	-	-	-	X	-	-	X	-	-	-	-	-	X	X	X	X	X	X	X
concentration																				
Oil concentration	X	-	-	-	X	-	-	X	X	X	X	X	X	X	X	X	X	X	X	X
SO ₄ ²⁻ by BaSO ₄	X	-	-	-	-	-	-	X	-	X	-	-	X	X	X	-	-	-	-	-
precipitation																				
SO ₄ ²⁻ by ion	-	-	-	-	-	-	-	-	X	-	X	X	-	-	X	X	X	X	X	X
chromatography																				
Solid phase analysis																				
LOI	X	-	-	-	-	-	-	X	-	-	-	-	-	-	X	X	X	X	X	X
DSC	X	-	-	-	-	-	-	X	X	-	X	X	-	-	X	X	X	X	X	X
QIR	X	-	-	-	-	-	-	X	X	-	X	X	-	-	-	-	-	-	-	-
Rheological properties																				
Mini slump	X	-	-	-	-	-	-	X	-	X	-	-	X	X	X	X	X	X	X	X
Set time	X	-	-	-	-	-	-	X	-	-	-	-	-	-	X	X	X	X	X	X
Heat of hydration																				
Conduction calorimetry	X	-	-	-	-	-	-	X	-	-	-	-	-	-	X	X	X	X	X	X

the mix water.

There were two mixes prepared with addition of different dosages of Na_2SO_4 . One mix was dosed with 0.6% of Na_2SO_4 , and the other mix with only 0.03%. To distinguish those mixes, the fourth supplemental code element was used, the latter mix was designated as WBN0.

In this research, the following parameters of the various cement pastes were determined by the analytical methods specified.

1. Loss on ignition by igniting a previously oven dried sample to 950°C for 15 minutes.
2. Amounts of ettringite and of calcium sulfate hydrates in the solids by Differential Scanning Calorimetry (DSC).
3. Amount of insoluble anhydrite in the solids by Quantitative X-ray Diffraction (QXRD).
4. Relative fluidity of paste by increase in area using the mini-slump cone.
5. Time of set of paste by Vicat apparatus.
6. Rate of heat evolution by the conduction calorimetry.

In addition, the following solution parameters were determined in paste solutions separated from the solids by pressure assisted filtration, or by use of a high pressure die, as appropriate:

7. Superplasticizer concentration in solution by UV spectroscopy.
8. K^+ , Na^+ , Ca^{2+} ion concentration of the liquid phase by atomic absorption spectroscopy.
9. OH^- ion concentration of the liquid phase by titration with HCl.
10. SO_4^{2-} ion concentration of the liquid phase either by $BaSO_4$ gravimetric method, or by ion chromatography.

For the pastes of the white cement W, the control paste WO without superplasticizer was investigated first. The inorganic ion concentrations in the pore solution were determined and the solids were analyzed by DSC and QXRD. The set time, mini-slump, and the heat of hydration were also measured.

The mix series WAX and WBX (X signifies a "wild card" character) were designed to investigate the effects of alkalis added to the mix water on this almost alkali-free cement. In this series, the effect of alkali hydroxides was specifically investigated by the mix series WAX. KOH was used as the alkali hydroxide added in the mix water, and its dosage was controlled to 0.3%, 0.45%, 0.6%, 0.9%, and 1.2% Na_2O equivalent of the cement weight (samples coded WA1, WA2, WA3, WA4, WA5, respectively). WA0 is a control mix without addition of KOH. The superplasticizer used in these mix WAX was the naphthalene sulfonate superplasticizer A and its dosage was 2% by solid weight of the cement. The residual superplasticizer concentration was analyzed.

In a subsequent series of mixes WBX, naphthalene sulfonate superplasticizer B was used, and its dosage was fixed as 1.55%. The mix WB0 was a control mix without any addition of alkali, and the same analyses done for the first blank mix WO were carried out and their results were compared.

The effects of added KOH were further investigated with superplasticizer B. The mix WB3 and WB5 are parallel mixes to WA3 and WA5, with addition of KOH in the mix water at the dosage of 0.6% and 1.2% Na_2O equivalent, respectively. The mix WB3' is a repeat of the mix WB3. The OH^- and SO_4^{2-} ions in solution and the CaSO_4 bearing phases in solids were determined for these mixes, as well as residual superplasticizer concentration.

The effects of added alkali sulfates were also investigated here. Two different kinds of alkali sulfates, K_2SO_4 , and Na_2SO_4 at the equal dosage of 0.6 % Na_2O equivalent were added in the mix water for the mix WBK and WBN. The inorganic ion concentrations and the superplasticizer concentration in pore solution were analyzed for these mixes. The mini slump measurement was also carried out. Their results can be also compared to those of the mix WB3, at the same 0.6% addition, and the different effects of KOH and alkali sulfates were discussed.

The mix WBN0 also contains Na_2SO_4 in the mix water but its amount was only 0.03% Na_2O equivalent. This mix was designed to investigate the effect of Na_2SO_4 impurity in the superplasticizer. The OH^- , SO_4^{2-} ion concentrations in solution, and CaSO_4 bearing phases were determined for this mix.

The sampling of the paste W series were continued for several hours; additional samples at 24 hours were taken only for the mix WO and WB0.

In the mix series LX, and SX, the effects of two kinds of superplasticizers on both solids and solution of the pastes of ordinary "gray" portland cement L, and S, respectively, were investigated. These cements contained different forms of calcium sulfate.

With ASTM Type I cement L, three mixes were designed; the control mix LO without superplasticizer; the mix LB with naphthalene sulfonate superplasticizer B at 1.55 % dosage; and the mix LM with melamine sulfonate superplasticizer M at 0.5 % dosage. For each of these, a complete set of analyses were carried out. Sampling was at reasonably close intervals during the first day, and then at 3 days, 7 days, and 14 days.

In the mix series SX, using ASTM Type I cement S, the mix SB (with 1.55 % naphthalene sulfonate superplasticizer B), and the mix SM (with 1.55 % melamine sulfonate superplasticizer M) were compared to the admixture-free mix, SO. Both the parameters analyzed and the duration of the sampling were almost the same as for mix series LX.

4.2 Mixing and Sampling

All cement pastes were mixed using a standard Hobart mixer, in accordance with the ASTM C 305 mixing procedure for cement paste. Where used, the superplasticizer and alkalis were pre-dissolved in the mix water. The water:cement ratio was kept as

0.50 throughout the research. A considerable volume of each paste was stored in a large container, and additional smaller portions placed in small ointment jars and sealed.

For analyses prior to set, the large mass was used as the sample source. At each sampling the container was opened and the sample stirred to insure homogeneity. A portion of about 50 g was then removed and the mix solution was recovered from the fresh paste by a pressure filtration system, illustrated in Fig. 4.2-1. Nitrogen gas pressure of 40 - 80 psi and the use of a membrane filter of 0.45 μm nominal diameter were found to be effective in recovering solution for analysis.

After set, individual portions set aside in sealed ointment jars were removed at appropriate intervals and subject to pore solution expression using the high pressure die system described by Barneyback and Diamond [8], and illustrated in Fig. 4.2-2. The specimen was set in the bore of the die body, followed by the teflon seal and the piston unit. Specimens were loaded in a testing machine at up to 80,000 psi. Around 5 ml pore solution were obtained easily from even the oldest specimen examined, 14 days old.

For each sample from which pore solution was removed, the solids were recovered by flushing the paste with acetone for later solid phase analyses.

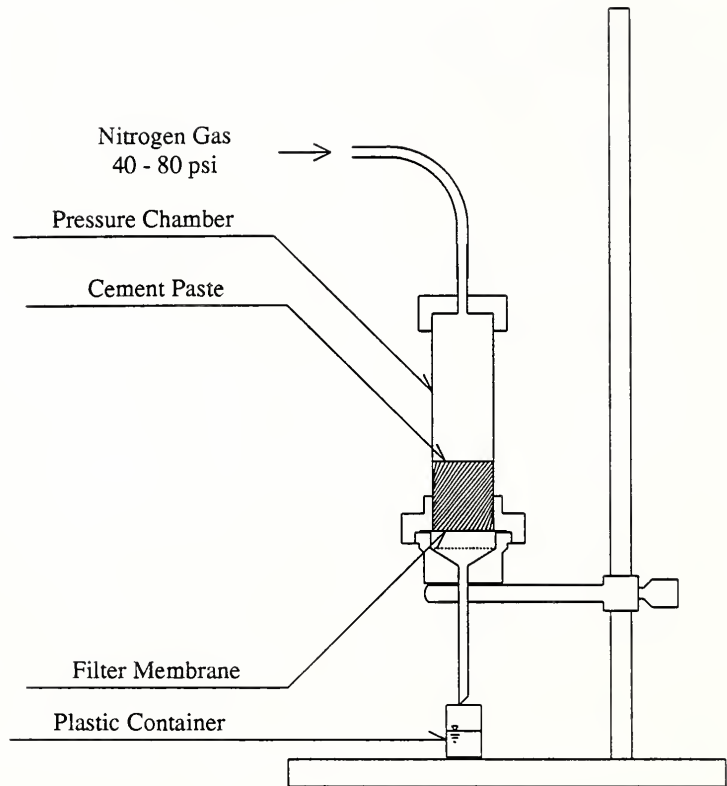


Fig. 4.2-1 Schematic drawing of pressure filtering system

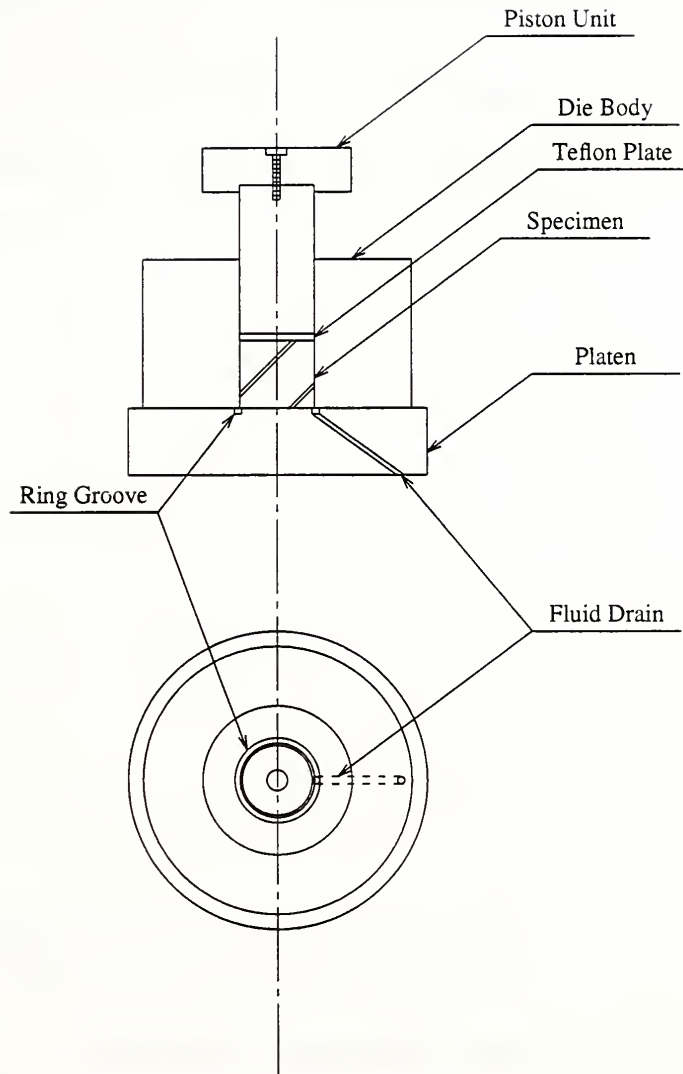


Fig. 4.2-2 Schematic drawing of steel die

4.3 Analyses of Solution Phase

4.3.1 Naphthalene Sulfonate Superplasticizer Measurement by UV Spectroscopy

The naphthalene sulfonate concentrations were determined by UV analysis procedure described by Diamond and Struble [67]. The instrument used was Varian DMS 200 UV-visible spectrophotometer. The UV scanning speed was 50 nm/sec and the slit width was 2.0 nm. The original pore solution was diluted with de-ionized water by usually 1:1000. The UV absorption spectra of the naphthalene sulfonate superplasticizers A and B are shown in Fig. 4.3-1. The concentrations of two superplasticizers used to obtain these spectra correspond to 1:2500 dilutions of 2.0% dosage for superplasticizer A and 1.55% dosage for superplasticizer B.

The absorbance A of the diluted solution was measured directly in the absorbance mode of the instrument. The equation ordinarily applied for calculation is Beer-Lambert Law written as,

$$A = \epsilon \cdot l \cdot c$$

where:

ϵ is the extinction coefficient (absorptivity) of a particular compound in a particular solvent at a particular wavelength in $L/g \cdot mm$.

l is the light path length, 10 mm for this study.

c is concentration in g/L .

The UV spectrum of the naphthalene sulfonate superplasticizers consists of two peaks, an intense absorption peak at approximately 228 nm and a much weaker peak in the

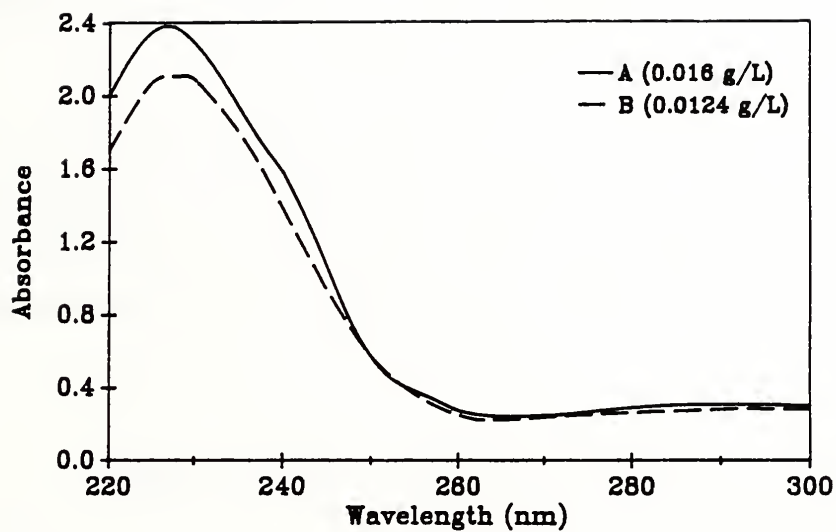


Fig. 4.3-1 UV absorption spectra of naphthalene sulfonate superplasticizers A and B

range between 270 nm and 294 nm, as shown in Fig. 4.3-1. Since the extinction coefficient of the monomer naphthalene sulfonate and that of the polymeric species at 228 nm peak are quite different, the calculation using the shorter wavelength absorbance requires correction for the proportion of the residual monomer. However, the extinction coefficient by using the peak at the longer wavelength do not vary with different degrees of polymerization for naphthalene sulfonate. Thus the complication of the monomer composition can be avoided when the unique value of the extinction coefficient at 270 - 294 band peak is used.

The average extinction coefficient of naphthalene sulfonate species at the long wavelength was determined as 2.20 L/g·mm from the known concentration cases of the superplasticizer A. The figure for the identical admixture was reported as 2.08 by Burk et al. [66], 2.26 by Diamond and Struble [67], and 2.18 by Struble and Rossington [68].

4.3.2 Melamine Sulfonate Superplasticizer Measurement Method

Melamine sulfonate concentration was also determined by UV analysis. The pore solution was diluted to 1:2000 with de-ionized water. The UV spectrum of the original admixture M is shown in Fig. 4.3-2. It has only one characteristic peak of absorption, which appears in the range between 210 and 220 nm.

This UV light absorption peak at 210 - 220 nm band is interfered with by OH^- ion, as pointed out by some researchers such as Massazza et al. [43], or Yilmaz et al. [69]. The absorbance in the range shorter than 220 nm is enhanced by the OH^- ion.

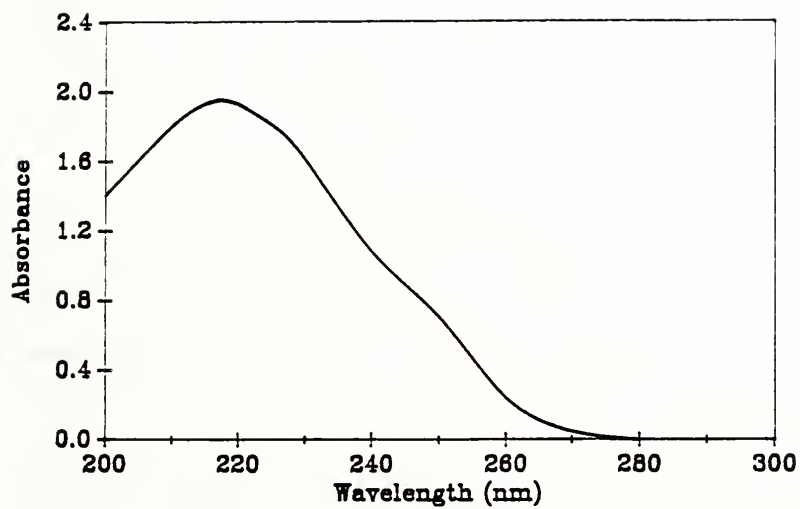


Fig. 4.3-2 UV absorption spectrum of melamine sulfonate superplasticizers M (0.02g/L)

and the peak is unable to be recognized in stronger alkaline solutions. To avoid this interference, the paste solutions were neutralized prior to the UV spectroscopy measurement with sulfuric acid. Sulfuric acid was found to exhibit less interference on absorption in this range than did hydrochloric acid or nitric acid. Fig. 4.3-3 illustrates the effect of neutralization by these three kinds of acid on a trial superplasticizer concentration determination in the pore solution of 1-day old sample. HNO_3 had a strong characteristic absorption over this range. HCl caused some enhancement of the absorption at 195 nm or lower wavelength. However, H_2SO_4 had no detectable interference on the absorption peak of the superplasticizer.

4.3.3 Determination of Inorganic Ion Concentrations

The major inorganic ions in the pore solutions, K^+ , Na^+ , Ca^{2+} , OH^- , and SO_4^{2-} , were determined by various methods. The details of each measurement are described below.

(1) Na^+ and K^+

The flame emission mode of an atomic-absorption - flame-emission spectrophotometer (Varian SpectrAA-20) was used for these alkali ions. In these determinations, the original pore solution was usually diluted 1:1000 to bring these alkali ion concentrations within in the calibration range, below 10 ppm for the Na^+ ion, and below 20 ppm for the K^+ ion. The operational conditions of the spectrophotometer for the element measurement are outlined in Table 4.3-1. Although Na and K are somewhat

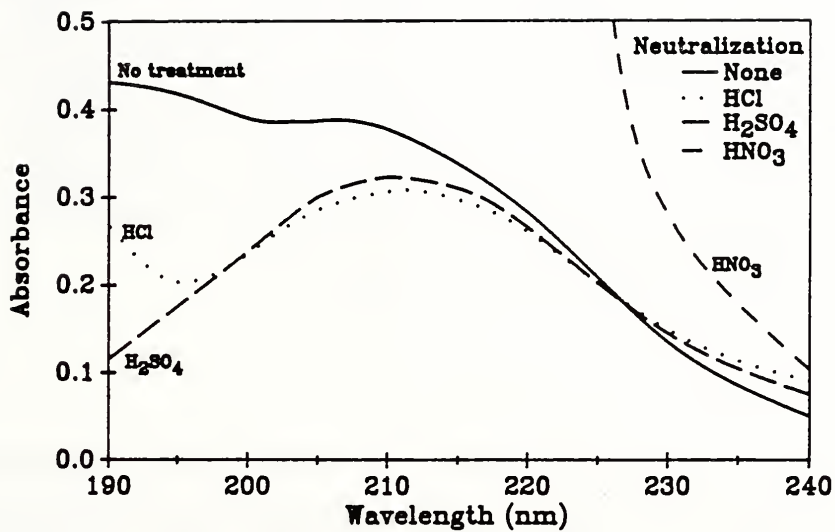


Fig. 4.3-3 Effects of the OH^- ion and neutralization with acids on UV absorption spectrum of melamine sulfonate superplasticizer M

subject to mutual ionization, common calibration standards for both ions without any additional reagent were used, according to the method of Barneyback [70].

(2) Ca^{2+}

The atomic absorption mode was chosen for Ca^{2+} using a $\text{N}_2\text{O}-\text{C}_2\text{H}_2$ flame. The operational parameters used are also listed in Table 4.3-1. The optimum working range for those operational conditions was 1-5 ppm. Prior work done by the author [71] showed some interference (to a maximum of about 15%) could be produced by varying matrices of different pore solutions. Since the Ca^{2+} concentration of pore solutions in this study did not exceed a maximum of 100 meq/L and this low values did not seem to affect the overall result, a single calibration standard solution contained only CaCO_3 was used.

(3). OH^-

OH^- ion was determined by titration with 0.06 N HCl acid. Methyl red was used as an indicator. After the solution reaches the first end point, it was boiled to expel CO_2 , and the titration was resumed to the second end point.

Table 4.3-1 Analytical condition used for elements measurement

Element	Na	K	Ca
Wave Length (nm)	589.0	766.5	422.7
Slit Width (nm)	0.5	1.0	0.5
Mode	FE	FE	AA
Hollow Cathode Lamp	--	--	Ca
Lamp Current (mA)	--	--	4
Fuel	C ₂ H ₂	C ₂ H ₂	C ₂ H ₂
Flow (l/min)	1.7	1.7	5.7
Support Gas	Air	Air	N ₂ O
Flow (l/min)	12.0	12.0	9.7
Stock Solution	NaCl Na ⁺ 1000ppm and KCl K ⁺ 1000ppm	NaCl Na ⁺ 1000ppm and KCl K ⁺ 1000ppm	CaCO ₃ Ca ²⁺ 1000ppm

(4). SO_4^{2-}

The sulfate ion was determined by two methods, direct BaSO_4 precipitation gravimetric method and ion chromatography. Indirect determination of SO_4^{2-} with the Ba^{2+} ion using atomic absorption was discarded due to the interference by naphthalene sulfonate remaining in the solution.

The BaSO_4 gravimetric method used was based on the ASTM C114 SO_3 determination procedure. This was mainly used in the early stages of this study, before the ion chromatography equipment became available. The contamination of BaSO_4 precipitate with naphthalene sulfonate was hardly avoidable when the residual polymer concentration was high, and its brownish color was frequently observed in the precipitate. Thus the method required monitoring of the residual naphthalene sulfonate concentration between each experimental operation, described as follows.

Two or three ml of the original pore solution was diluted to 250 ml, acidified with HCl, and digested for 15 minutes at a temperature just below boiling. Ten ml of BaCl_2 (100g/L) were added slowly to the solution, while was then heated for 15 minutes more. The solution was then left for 12 -18 hours to complete the precipitation of BaSO_4 . It was then filtered through a medium speed glasswool filter, and the precipitate was oven dried at 105°C and weighed. At the same time, the concentration of naphthalene sulfonate in the filtrate was determined by UV spectroscopy.

The BaSO_4 precipitate consumed all the sulfate ion, and also a part of the naphthalene sulfonate polymer anion. An analysis for the latter was obtained by the

subtraction of the final concentration in the filtrate from the initial concentration. The calculation algorithm for the actual SO_4^{2-} ion concentration is illustrated on the following page. The result of a trial determination of a known SO_4^{2-} ion concentration in a synthetic pore solution with superplasticizer added was reasonably accurate with only $\pm 0.3\%$ difference.

In the later stages of this study, an ion chromatography method was applied for analysis of SO_4^{2-} concentrations. This method provides for a direct determination of SO_4^{2-} ion concentration regardless of the remaining superplasticizer in the solution. The instrument used was a Dionex 2000i/SP ion chromatography and equipped with an automatic integrator for the peak area calculation. The parameters of the instrument for this study are summarized in Table 4.3-2.

The calibration standards used contained 5 ppm and 10 ppm of the SO_4^{2-} ion in Na_2SO_4 solution. The original pore solution was diluted to the SO_4^{2-} ion calibration range, usually by 1:1000 or 1:2500. The electrical conductivity was measured and automatically recorded as a function of time. The retention time for the sulfate ion under this particular settings of the instrument was around 6 minutes. Other than the SO_4^{2-} ion, the pore solution contained the OH^- ion, and the naphthalene sulfonate polymer anion as well. Neither anion is responded to by this chromatography system. The peak area of the conductivity is thus proportional to the SO_4^{2-} concentration, which was automatically calculated by the integrator.

$$W_{[NS]^-} = (C_o - C_r) \times V_s$$

$$W_{Ba[NS]} = W_{[NS]^-} \times \left(1 + \frac{cd_{NS}}{1000} \times [Ba \text{ equiv.}] \right)$$

$$W_{BaSO_4} = W_{prcp} - W_{Ba[NS]}$$

$$C_{SO_4} = \frac{W_{BaSO_4}}{[BaSO_4 \text{ equiv.}]} \times \frac{1000}{V_s}$$

where:	$W_{[NS]^-}$;	weight of naphthalene sulfonate in precipitate (g)
	C_o ;	original concentration of naphthalene sulfonate anion in pore solution (g/L)
	C_r ;	residual concentration of naphthalene sulfonate anion after filtration (g/L)
	V_s ;	pore solution sample quantity (L)
	$W_{Ba[NS]}$;	weight of Ba-[naphthalene sulfonate] in precipitate (g)
	cd_{NS} ;	charge density of naphthalene sulfonate (meq/g)
	[Ba equiv.] ;	weight of Ba equivalent (137.33/2 g/eq)
	W_{BaSO_4} ;	weight of $BaSO_4$ (g)
	W_{prcp} ;	weight of total precipitate (g)
	C_{SO_4} ;	concentration of SO_4 in pore solution (meq/L)
	$[BaSO_4 \text{equiv.}]$;	weight of $BaSO_4$ equivalent. (116.7 g/eq)

SO_4 calculation procedure by $BaSO_4$ gravimetric method

Table 4.3-2 Parameters for ion chromatography instrument

Anion Separator	
Flow Rate	2.0 mL/min
Flow Pressure	1000 psi
Eluent	2.8 mM NaHCO ₃ 2.2 mM Na ₂ CO ₃
Regenerent	25 mN H ₂ SO ₄
Sample Volume	0.75 mL

The reproducibility was such that the fluctuation of the peak area was within a 3% coefficient of variation. In comparisons made between the two methods of SO_4^{2-} analysis, it was found that the means of results by the BaSO_4 gravimetric method and by ion chromatography corresponded to each other within 4.0%. However, the ion chromatography method is recommended because of the much simpler experimental procedure.

4.4 Analyses of Solids

4.4.1 Loss on Ignition

The loss on ignition of the cement solids was determined according to ASTM C114. One gram of cement paste was ignited in a crucible in the muffle furnace at $950 \pm 50^\circ\text{C}$ for 15 minutes. Then it was cooled to the room temperature and reweighed. The ignition loss data for the solids with superplasticizers were corrected for the weight of the superplasticizer absorbed at each time of sampling.

4.4.2 Differential Scanning Calorimetry (DSC)

The instrument used was Du Pont 910 thermal analysis system. The DSC mode was chosen among other thermal analyses methods because of the greater sensitivity of the enthalpy measurement, and because the smaller sample size gives more facility to the experimental procedure. Quantitative analysis was carried out for ettringite ($\text{C}_3\text{A}\cdot 3\text{C}\bar{\text{S}}\cdot 32\text{H}$), calcium sulfate hemihydrate, and gypsum by measuring the areas of

the respective dehydration peaks. Other hydrated compounds in cement pastes such as C-S-H gel were also observed in the DSC curve.

A synthetic ettringite for calibration was made by the following method described by Struble [72]. A stoichiometric amount of $\text{Al}_2(\text{SO}_4)_3$ solution was added to a saturated calcium oxide solution, upon which a white precipitate of ettringite appeared immediately. The ettringite was filtered and dried under flowing of nitrogen gas to avoid carbonation. An x-ray diffraction pattern of this synthetic ettringite showed no peaks other than those expected for ettringite.

The calibration material for calcium sulfate hemihydrate was obtained in ground form from Texas Industries Inc.. Originally this sulfate was natural gypsum mined by the U.S. Gypsum Corp. in Sweetwater, Texas. The hemihydrate was apparently synthesized by heating the gypsum. Its purity was assured by its x-ray diffraction pattern, which showing diffraction peaks only for hemihydrate, and by a thermogravimetric analysis (TGA), which showing weight loss equivalent to an approximate half mole of water.

Reagent grade of gypsum was used for gypsum calibration. This gypsum is 99.99% pure.

Another common form of CaSO_4 is soluble anhydrite ($\gamma\text{-CaSO}_4$). It has only a trace of combined water and its crystal structure is almost identical to calcium sulfate hemihydrate. X-ray diffraction patterns of these two compounds are hardly distinguishable from each other. It was found here by DSC analysis that a soluble anhydrite

synthesized by heating gypsum to over 120°C, rehydrated to hemihydrate immediately in an atmosphere at the normal level of humidity (ca. 50% R.H.). This rehydration phenomenon has been generally observed for example by McAdie [73], Gay [74], and Hansen et al. [63]. Soluble anhydrite may exist in unhydrated cement as a result of dehydration of gypsum during the grinding operation. However, this soluble anhydrite in cements is considered to be mostly converted to hemihydrate. From these reasons, soluble anhydrite was not determined in this study.

The DSC analysis procedures used were as follows. The acetone dried solid sample was passed through a No. 325 sieve (0.045 mm), and ca. 4.0 mg of the sieved solids was placed in the aluminum pan of the instrument. The weight of the specimen used was reduced to about 1.5 mg when higher resolution was needed for separation of close peaks. The sample pan was then placed in the sample chamber along with the empty reference pan. Both pans were left open. It was found by extensive prior investigation that either crimping or hermetically sealing caused poor reproducibility of the dehydration peak temperatures.

It was found that the water content of the purging gas passed into the sample chamber affected the temperature of the dehydration peak. Air of 10 % relative humidity at room temperature was chosen as the purging gas. Its flow rate was set at 140 mL/min. It was found that these conditions of the purging gas gave the best separation of the dehydration peaks of calcium sulfate hemihydrate, gypsum, and ettringite, and this was used. The relative humidity was controlled by bubbling the air through a glycerine-water solution, by which a constant relative humidity was maintained as

described in ASTM E 104-51.

A heating rate of 10°C/min was chosen as providing the best resolution of adjacent dehydration peaks.

Some of the solid samples analyzed contained all three compounds: ettringite, hemihydrate, and gypsum. The DSC curve for one of them, paste LB at age of 16 minutes, is shown in Fig. 4.4-1 to provide an example. The three peaks in the figure are characteristic DSC dehydration peaks for ettringite, calcium sulfate hemihydrate, and gypsum, respectively. These were observed in increasing order of temperature under these particular conditions of the purging gas, the sample preparation, and the heating rate.

The ettringite synthesized here had its DSC dehydration peak between 40°C and 50°C, in approximate agreement with the temperature range found by Struble et al. [72], which ranged from 30° to 55°C. Ettringite found in actual solids cement pastes at early ages started its dehydration approximately 35°C. As hydration proceeds or if large specimen weights were used, the dehydration peak tends to shift to higher temperature, ranging in this case from 40°C to 80°C.

The calcium sulfate hemihydrate used for calibration had its dehydration peak at approximately 80°-90°C, between which a half mole of combined water was released. Hemihydrate found in actual unhydrated or hydrated cements exhibited its dehydration peak at about the same temperature.

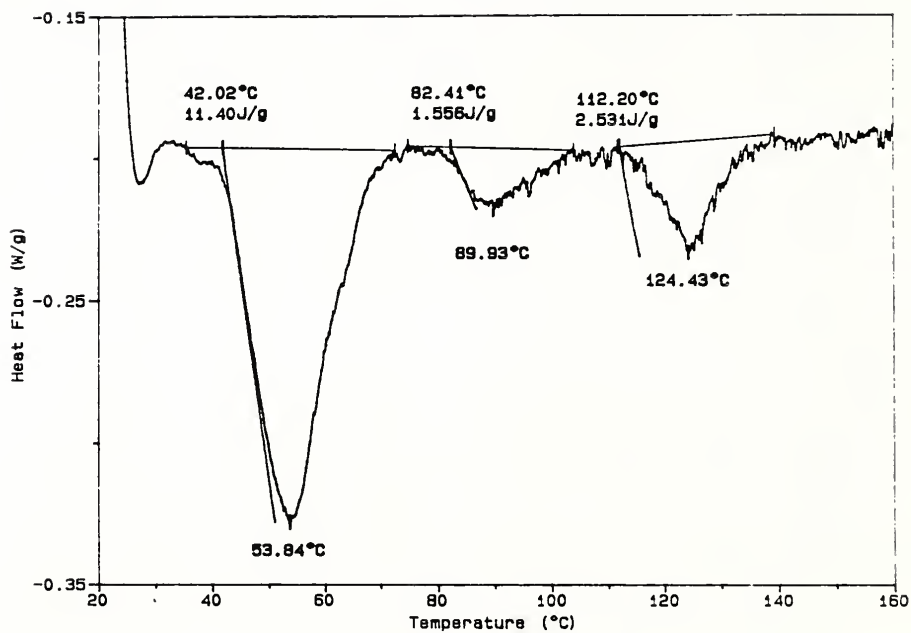


Fig. 4.4-1 DSC curve of paste LB at age of 16 minutes

The dehydration peaks of both pure gypsum and gypsum in actual cement and cement paste solids were observed in the range between 110°C and 120°C. Under the experimental conditions used, the entire two moles of its combined water were removed at once, in a single step.

The calibration curve for ettringite was obtained by a series of mixtures of the synthesized ettringite and a cement matrix, which does not have a peak in the corresponding temperature range. The three mixes containing 5%, 10%, and 14% of ettringite, along with 100% ettringite were used for this calibration curve determination. Fig. 4.4-2 shows the calibration curve obtained.

The calibration curves for hemihydrate and for gypsum were obtained similarly. For hemihydrate calibration, a series of mixtures contained 3%, 5%, and 6% of hemihydrate, plus 100% pure hemihydrate were used. For gypsum calibration, the gypsum contents of the mixtures used were 5%, and 6%, and 100% pure sample was also used. These curves are shown in Fig. 4.4-3 and Fig. 4.4-4.

According to the results of those calibrations, the average areas of the dehydration peaks of pure ettringite, hemihydrate, and gypsum under the particular settings of the instrument corresponded to about 810, 180, and 630 joules/g, respectively. The contents of these compounds in each solid sample were determined by normalizing the areas of corresponding dehydration peaks to those calibration numbers for pure compounds.

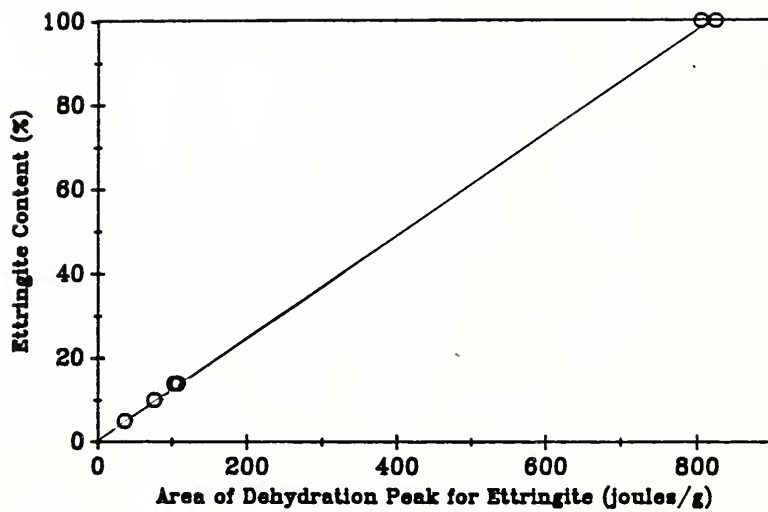


Fig. 4.4-2 Calibration curve for ettringite content by DSC dehydration peak area

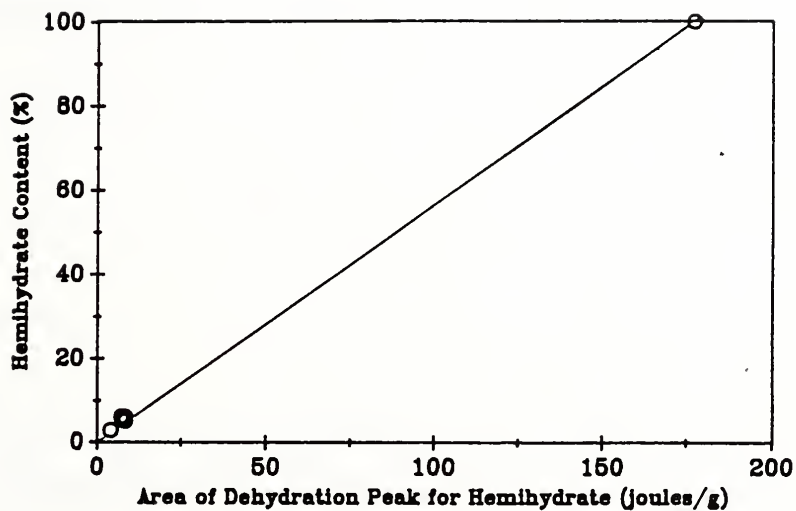


Fig. 4.4-3 Calibration curve for hemihydrate content by DSC dehydration peak area

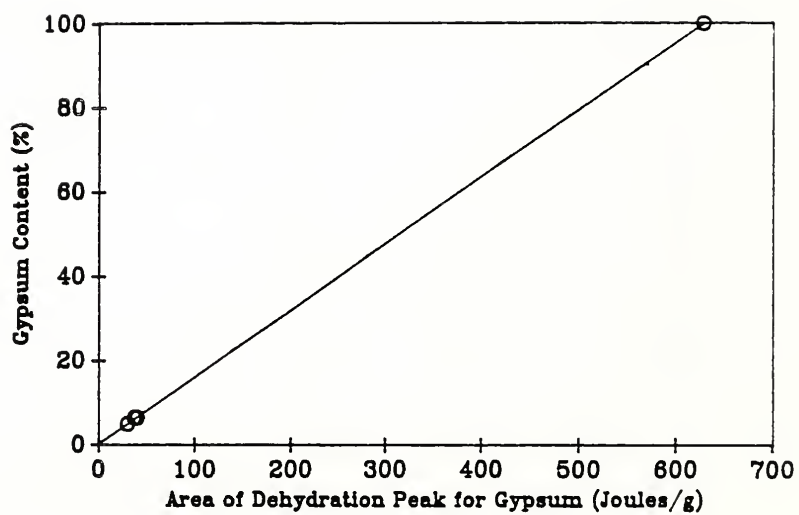


Fig. 4.4-4 Calibration curve for gypsum content by DSC dehydration peak area

The starting point and end point of the dehydration peak on the DSC curves were defined generally as the points where the gradient of the curve changes abruptly. These points were determined by inspection, or sometimes with some help from derivative curves provided by the instrument. The peak area under the straight line between those two points was calculated automatically by a computer program attached to the instrument.

A major hydration product of cement, C-S-H gel, loses its combined water at relatively low temperatures. A trial run of a synthetic C-S-H gel produced by hydration of a pure C_3S exhibited a broad DSC dehydration peak ranging from $40^\circ C$ to $180^\circ C$. This temperature range overlaps the peaks of ettringite, hemihydrate, and gypsum. However, peaks of these target compounds are much sharper, so that they can be differentiated from the broad hump of the baseline caused by C-S-H gel.

Another source of complication is the formation of AFm phases in the cement pastes after several days. X-ray diffraction analysis was carried out for all specimens made with cement L and cement S aged between 1 day and 14 days. In none of these was an x-ray diffraction peak for calcium monosulfoaluminate hydrate ($C_3A \cdot \bar{C}\bar{S} \cdot 12H$, d-spacing: $9.0\text{\AA}$) observed. However, in some of the pastes, small and poorly defined x-ray diffraction peaks at about $7.9\text{\AA}$ were developed typically starting at 3 days. These are likely to be due to C_4AH_{13} or sometimes in part to a partly carbonated phase of similar structure ($C_4A\bar{C}\bar{O}_{0.5}H_{12}$).

With respect to DSC, the author has examined a pure specimen of the calcium monosulfoaluminate hydrate under the same experimental conditions and found that it has a complex response; broad complex peaks between about 40°C and 110°C, and a well defined peak between about 130°C and 180°C. Thus if this compound were present in the experimental pastes, the first peak would contribute to the peak normally attributed to ettringite. However, the absence of any indication of an x-ray diffraction peak at or near 9.0Å, it must be concluded that it is absent.

The author has also examined the DSC response for old reference samples of C_4AH_{13} . Unfortunately, these were carbonated to some degree, shown peaks for vaterite, aragonite, and calcite as well as the 7.9Å peak characteristic of C_4AH_{13} . The DSC response for these samples involved small peaks between 80°C and 130°C and a much larger response at high temperature (230°C to over 300°C). The normal limits of the ettringite DSC peak with the technique used is about 40°C to 90°C; hence these could have produced some slight augmentation of the ettringite peak by the low temperature peaks here. However, all runs of actual solid samples were carried out at least to 300°C and there was no indication of the large expected second peak. Thus the situation is ambiguous, the assay of ettringite at later ages in those pastes may have included a very small contribution from the C_4AH_{13} indicated to be present by x-ray diffraction.

The DSC peaks for some specimens, notably those for cement S with naphthalene sulfonate (SB) and melamine sulfonate (SM) admixtures, and for cement L with melamine sulfonate admixture (LM) show distinct shoulders on the high temperature

side of the peak, ca. 90°C. However, the existence of those shoulders does not correlate with the existence of the previously mentioned 7.9Å x-ray diffraction peak, and the shoulders are thought to represent primarily the effects of absorbed superplasticizer.

4.4.3 X-ray Diffraction Analysis

The instrument used was a Siemens D500 diffractometer using Cu-K α radiation. The goniometer speed ordinarily used was 2° 2 θ /min.

All the dry powdered sample material used was passed through a No. 325 sieve (0.045 mm) and either packed in a McCreary mount, or sprinkled onto a quartz crystal mount when the sample amount was limited.

4.4.4 Quantitative X-ray Diffraction Analysis

A quantitative x-ray diffraction analysis procedure was applied for insoluble anhydrite (α -CaSO₄, or natural anhydrite) in pastes made with the white cement (cement W). This cement contains only insoluble anhydrite as the calcium sulfate present, and no other quantifiable method of analysis is available.

The instrument used and all the parameter settings were as described previously. The internal standard method was applied using CaF₂ as the internal standard and soluble starch (C₆H₁₀O₅)_x, as the matrix. The insoluble anhydrite, CaF₂, and (C₆H₁₀O₅)_x used for calibration were all reagent grade.

The insoluble anhydrite diffraction peak of d-spacing $3.499 \text{ \AA}$ (2θ of 25.4°) and the CaF_2 diffraction peak of d-spacing $3.155 \text{ \AA}$ (2θ of 28.3°) were used. Both diffraction peaks were strong and were found to be the least interfered by other peaks of cement compounds or hydrated cement products. CaF_2 at a uniform 20% by weight was added to each dry powdered sample. The combined powders were mixed in a plastic vial by shaking manually, and the mixture was passed through a No.325 sieve (0.045 mm) before being packed in a McCreary mount. Three replicate runs were carried out for each mixture.

The intensity ratio, that is, the ratio of the height of the specific peak of insoluble anhydrite to that of the CaF_2 peak is proportional to the weight composition of insoluble anhydrite. The calibration curve was obtained by a series of samples of CaF_2 :matrix weight ratio of 1:99, 3:97, and 5:95, and yielded a regression coefficient $R = 0.971$.

4.4.5 Tests on Physical Characteristics of Pastes

Physical characteristics of the cement pastes were monitored by the mini-slump test and by determination of the setting time based on ASTM C 191 procedure.

(1) Mini-Slump Test

The mini-slump cone test was described in detail by Meyer and Perenchio [58], and by Kantro [75]. Cement paste is transferred to the mini-slump cone and the cone is lifted smoothly and quickly. The area of the paste spread on a polyethylene sheet is

measured and the slump value is expressed as the ratio of the spread area to the original inner area of the cone, expressed in percentage terms.

(2) Setting Time

The setting time of various pastes was measured using the Vicat needle apparatus. The procedure complied essentially with ASTM 191. The actual penetration test was performed on paste in the ointment jars.

4.4.6 Conduction Calorimetry

The heat evolutions at early ages for the mix series WX, LX, and SX, were determined calorimetrically. The instrument used was a conduction calorimeter made by Wexham Developments Limited. The specimen used consisted of a hand mixed cement paste of 5 g cement and 2.5 ml of liquid contained in a polyethylene bag. The bag was positioned around the thermal sensor of the instrument in an aluminum can filled with non-conducting oil. This aluminum can, covered with thermal insulator, was assembled and placed in a sealed acrylic cylinder, which was there immersed in the water bath used as a constant temperature heat sink.

The electrical output from the thermal sensor, E (mV), was recorded by the plotter as a function of time. The relation between E and the heat evolution rate of the sample, W (mW) is written in the following Tian-Calvet equation.

$$W = K_1 \cdot E + K_2 \cdot \frac{dE}{dt}$$

Both K1 and K2 are constants of the instrument, and those constants were determined as

$$K1 = 29.05$$

$$K2 = 5.55$$

for the particular instrument of this study by Dr. D. Bonen of this laboratory. The results were expressed in units of mW/g of cement. The measurement was continued until the second peak of the heat of hydration was completed, usually by one and a half days.

CHAPTER FIVE

EFFECTS OF NAPHTHALENE SULFONATE SUPERPLASTICIZERS ON WHITE CEMENT "W" PASTES

In this chapter, effects of naphthalene sulfonate superplasticizers on cement pastes prepared with ASTM type I white cement (Coded cement W in this report) were investigated. This white cement has a very low alkali content, a low content of C_3A , and almost no C_4AF . Thus it is suitable as a "blank" material, since those parameters were considered to affect the interaction between dissolved superplasticizer and hydrating cement.

In Section 5.1, the results of a comprehensive study of (a) the control mix without superplasticizer (coded WO), and (b) a mix coded WB0, incorporating 1.55% naphthalene sulfonate superplasticizer B by weight of cement, are presented. Effects of naphthalene sulfonate are examined on various aspects of the paste including hydration, calorimetry, rheology, solution chemistry, and solid phase compounds formed.

In Section 5.2, specific effects of different alkali salts on absorption behavior of naphthalene sulfonate superplasticizers in cement W pastes were investigated. Two different naphthalene sulfonate superplasticizers (A and B) were used. Various kinds

and dosages of alkali hydroxides and alkali sulfates were dissolved in the mix water along with the naphthalene sulfonate superplasticizers. These series of mixes were coded WAX or WBX, depending on whether superplasticizer A or B was used. X is a wild card character which stands for the kinds or the dosage of the dissolved alkali. In this portion of the work, the main focus was to determine the effects of various treatment plus combination on the amount of superplasticizer remaining in solution after various periods. UV analysis of the residual naphthalene sulfonate in solution is the main analytical method.

In Section 5.3, some peculiar experimental findings in the previous series of pastes with superplasticizer A are re-investigated using superplasticizer B. Three pastes with cement W and 1.55% superplasticizer B were designed; one with 0.6% KOH, a second with 1.2% KOH, and a third with 0.03% Na_2SO_4 . For those pastes, the concentrations of remaining superplasticizer, the OH^- ion, and the SO_4^{2-} ion in pore solution were determined prior to set, and analyses of CaSO_4 -bearing compounds in the solids were also carried out.

In Section 5.4, based on the results of experiments described in the previous three sections, the superplasticizer interactions with the various pastes of this white cement W are discussed and explanations attempted. Differences in results with the two different naphthalene sulfonate superplasticizers are also discussed.

In Section 5.5, results of an experiment on the paste with melamine sulfonate superplasticizer M are reported. Effects of the melamine sulfonate superplasticizer on

the white cement was investigated to a limited extent, so the experimental results presented here are only for reference.

5.1 White Cement Systems with and without Superplasticizer B

5.1.1 Effect of Superplasticizer on Hydration

Fig. 5.1-1 shows the ignition loss data of the control mix WO and mix with superplasticizer WB0. All data for superplasticized pastes were corrected for the loss on ignition of the superplasticizer incorporated with the solids. With superplasticizer B, the loss on ignition (LOI) at the first measurement was a little higher than the control paste. However, it remained approximately constant for about 6 hours, while the LOI of the control pastes increased steadily; the control paste LOI overtook that of the superplasticized paste at about 3 hours and it was significantly higher by 6 hours.

Fig. 5.1-2 shows the conduction calorimetry results of both pastes. For the paste with superplasticizer, the start of the second heat evolution peak was delayed by 3 hours and the area under the peak was considerably reduced. This indicates that the superplasticizer retarded the overall hydration of cement W.

The rheological characteristics of the two pastes, as measured by the mini-slump cone percentage increase in area (or "spread") are shown as functions of time in Fig. 5.1-3. With this cement, it appears that the superplasticizer actually reduced the fluidity of the cement paste, the initial values of mini-slump spread being about 350%

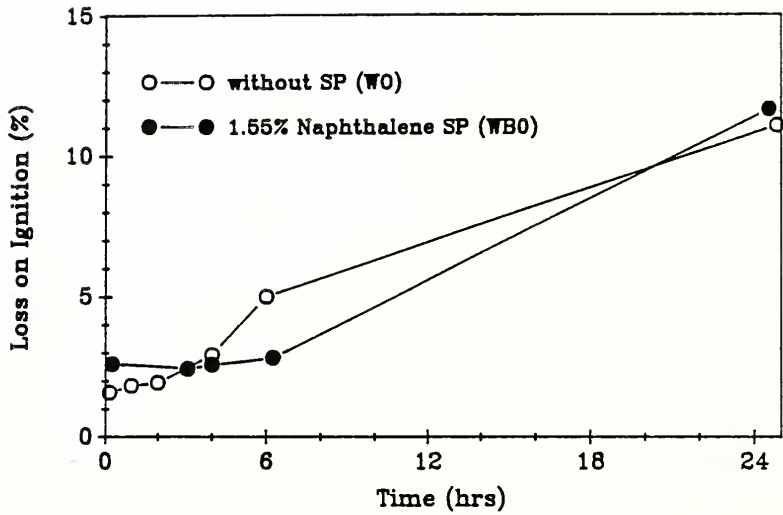


Fig. 5.1-1 Loss on ignition as a function of time up to 1 day for pastes of cement W without superplasticizer (WO) and with 1.55% naphthalene sulfonate (WB0)

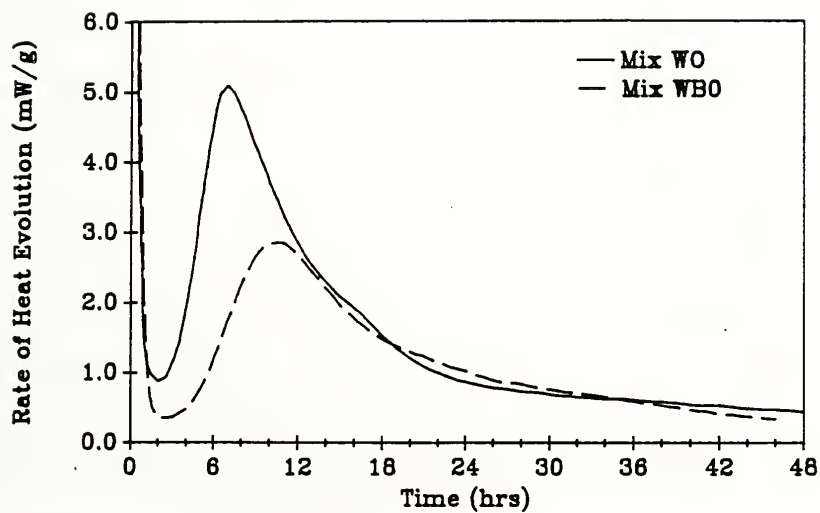


Fig. 5.1-2 Conduction calorimetric curves showing heat evolution vs. time for mixes WO and WB0

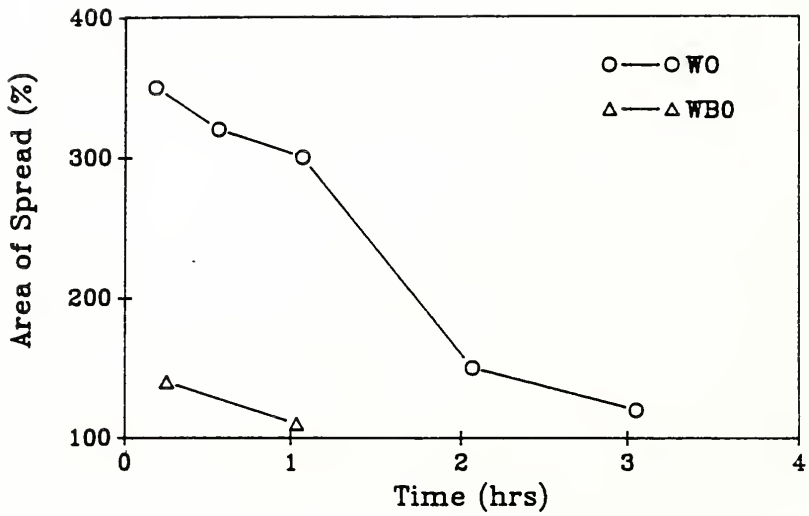


Fig. 5.1-3 Area of spread in mini-slump test vs. time for mixes WO and WB0

without the superplasticizer and only about 140% with it. Furthermore with the superplasticizer the spread was rapidly reduced to the base level (100%) while the cement paste without superplasticizer retained the ability to spread for up to 3 hours. It was observed that the superplasticized paste became gelatinous after only about 15 minutes in an initial "watery" state. No bleed water was detected.

Separate initial set time measurements for these pastes yielded a value of 5.5 hours for the control paste, and 6.5 hours for the superplasticized paste.

5.1.2 Control Paste Without Superplasticizer (WO): Solution and Solid Phase Analysis

5.1.2.1 Inorganic Ion Concentrations in the Paste Solution

Fig. 5.1-4 shows the concentrations of K^+ , Na^+ , Ca^{2+} , OH^- , and SO_4^{2-} ions in the solution phase as functions of time over the first 24 hours. For ages before 5.5 hours, the solution phases was separated from the solid by pressure-assisted filtration. As indicated in the figure, for ages of 5.5 hours and beyond, separation was accomplished using the high pressure die.

The sum of the inorganic ion concentrations in the pore solution was significantly smaller than that found in ordinary portland cement systems. It is an unusual observation that the Ca^{2+} ion was most concentrated of all the ionic species for the first 5 hours of hydration. These are reflections of the cement having a very low alkali content.

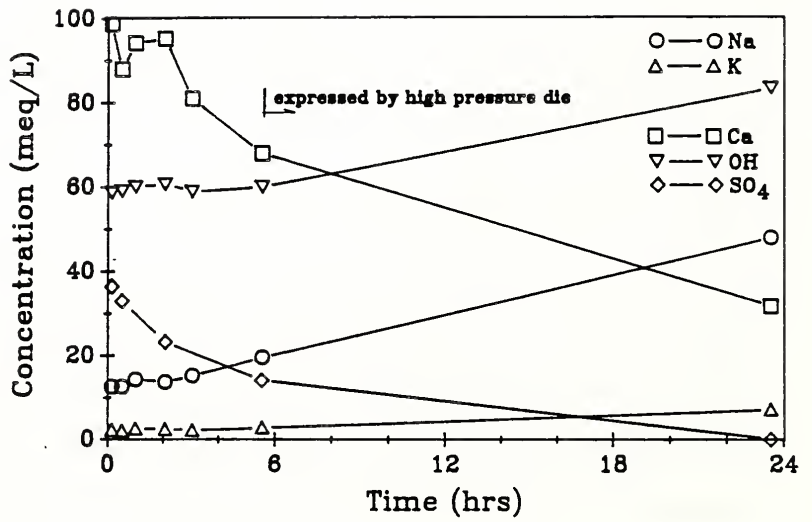


Fig. 5.1-4 Concentration of inorganic ions in mix water and pore solution vs. time in control paste (WO)

The sulfate ion concentration decreased monotonically throughout this period; it did not maintain constant concentration for some hours, as is usually found with ordinary portland cement pastes. The OH^- ion concentration was also low.

5.1.2.2 Solid Phase Analyses

Fig. 5.1-5 shows the results of analysis for calcium sulfate-bearing phases in the corresponding solids for the control paste WO, as functions of time over the first 24 hours. The y-axis expresses the concentration of each of the specific compounds (ettringite and anhydrite) in terms of its SO_4 content normalized to the ignited weight of the cement paste, so that these numbers are directly comparable each other. The content of anhydrite (insoluble or "natural" anhydrite) was determined by QXRD, and the ettringite content was determined by DSC. Details of the analytical methods used were presented in the previous chapter. The content of these compounds in the starting cement are indicated by filled-in data points. An analogous convention will be followed throughout this report.

The initial form of CaSO_4 in cement W is considered to be entirely insoluble anhydrite from the following indications. For the DSC curve of the unhydrated cement, there was no dehydration peak up to 300°C . From the X-ray diffraction pattern, peaks of calcium sulfates other than insoluble anhydrite were not observed. Diffraction peaks for alkali calcium sulfates were not recognized either. From the hydrated paste sample, only insoluble anhydrite and ettringite were the CaSO_4 -bearing phases detected up to one day.

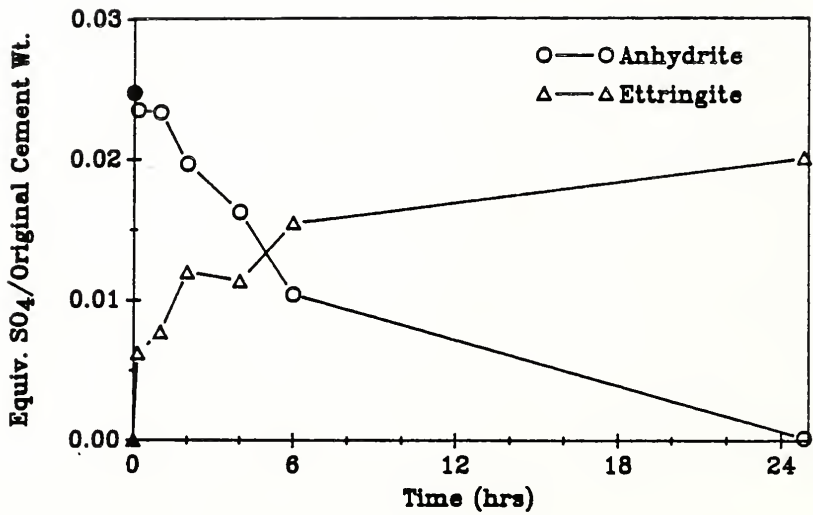


Fig. 5.1-5 Content of sulfate-bearing phases in paste solids vs. time up to 1 day for control paste WO
(Percentage of each solid phase re-expressed in terms of its SO₄ content.)

The anhydrite content in the control paste WO was hardly reduced at the first contact with water. However, it decreased monotonically between 1 and 6 hours, and there was virtually no anhydrite detected by 24 hours. No plateau period was evident in the anhydrite content pattern with time.

The content of ettringite, starting at zero, exhibited an immediate rise, evident by the analysis at 10 minutes. Then it continued to increase at a somewhat slower rate, and it reached about 2% equivalent SO_4 at 24 hours.

Table 5.1-1 shows the balance of the sulfates accounted for at each age. The SO_4 content of the original cement W is 3.76% by chemical analysis carried out by the author, whereas the initial anhydrite content determined by QXRD was around 2.5% of SO_4 equivalent. Some of this difference could be attributed to the sulfate forms in unhydrated cement which were not accounted for, such as alkali sulfate or alkali calcium sulfate. However, the alkali content of the cement W is only 0.083%, equivalent to 0.13% SO_4 if all alkali exists as a form of sodium sulfate. Thus it seems that the anhydrite amount calculated is somewhat low due to some complication of QXRD method.

The sum of the sulfates measured for sulfate-bearing compounds in the solid plus the sulfate ions in solution increased after the contact with mixing water and reached maximum of 3.23% SO_4 content at 2 hours. It then decreased. After the dormant period, considerable sulfate is incorporated into amorphous C-S-H gel, which was not quantified in this analysis. The decrease in the sum of the sulfates after 2 hours seems

Table 5.1-1 Total balance of sulfate-bearing phase for mix WO*

(Percentages expressed in terms of equivalent SO_4 content)

Age (hr)	Anhydrite (%)	Ettringite (%)	Σ Solid (%)	Solution (%)	Total (%)
0.00	2.47	0.0	2.47	0.0	2.47
0.17	2.35	0.62	2.97	0.09	3.06
1.00	2.33	0.77	3.11	0.08	3.19
2.00	1.97	1.20	3.17	0.06	3.23
4.00	1.62	1.13	2.76	-	-
6.00	1.04	1.55	2.59	0.03	2.62
24.83	0.01	2.01	2.03	0.00	2.03

* The total SO_4 content of the cement, separately determined, was 3.76% as SO_4 .

to be due to this effect.

5.1.3 Paste with Naphthalene Sulfonate Superplasticizer B (WB0): Solution and Solid Phase Analysis

5.1.3.1 Removal of Superplasticizer from Solution

Fig. 5.1-6 indicates the concentration of superplasticizer remaining in solution as a function of time up to 1 day for the paste with 1.55% naphthalene sulfonate superplasticizer B (WB0). Almost all the absorbable portion of superplasticizer B was removed from the solution by 3 hours, and the solution concentration remained low indefinitely.

5.1.3.2 Inorganic Ion Concentrations in the Paste Solution

Fig. 5.1-7 shows the changes in the inorganic ion concentrations up to one day for the mix WB0. In contrast to the control paste, the sum of the inorganic ion concentrations in the solution here was significantly higher. This was due to an additional 120 meq/L of the Na^+ ion derived from the superplasticizer, and to the OH^- ion that was found to balance this extra Na^+ . The sodium cation had previously been balanced by polymer anion groups (sulfonate groups) of the superplasticizer.

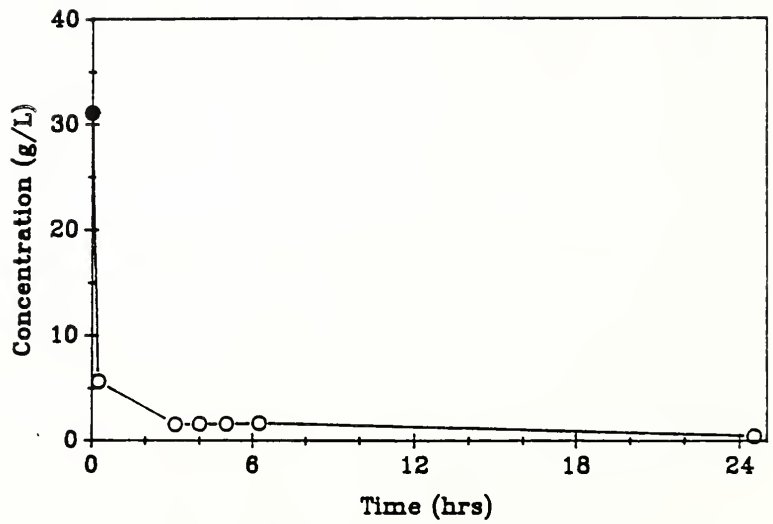


Fig. 5.1-6 Concentration of residual superplasticizer in mix water and pore solution for naphthalene sulfonate bearing pastes (WB0) up to 1 day

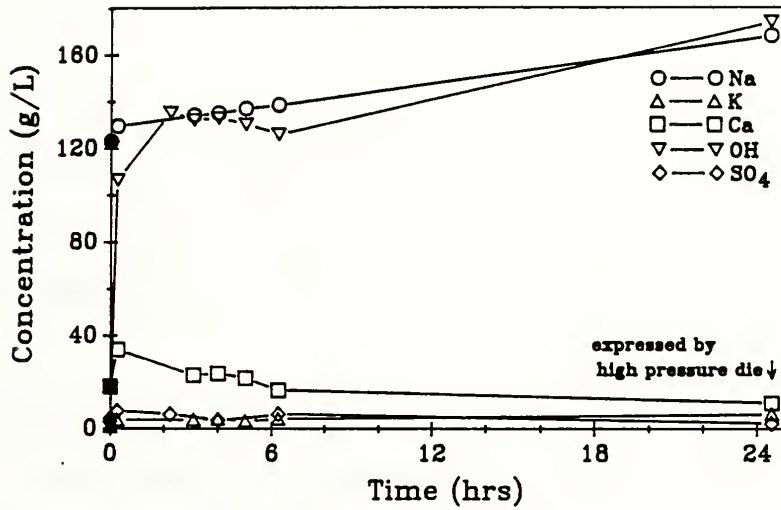


Fig. 5.1-7 Concentration of inorganic ions in mix water and pore solution vs. time in paste with naphthalene sulfonate superplasticizer (WB0)

The Ca^{2+} ion concentration here was much lower than in the control paste over the entire period of 1 day. The initial Ca^{2+} ion concentration was only 18 meq/L and it rose to a maximum of 35 meq/L at 16 minutes, before subsequently declining.

The SO_4^{2-} ion concentration was also found to be very low; it was less than 10 meq/L for the whole period of analysis, which was much lower than the control case for the first few hours.

5.1.3.3 Solid Phase Analysis

Fig. 5.1-8 shows the corresponding figure to Fig. 5.1-5 for the superplasticized paste WB0. Again insoluble anhydrite and ettringite were the only CaSO_4 -bearing phases detected. The peculiar quick setting behavior of the paste WB0 reported earlier, was not a false set, because the formation of gypsum was not observed either by X-ray diffraction or by DSC analysis.

The anhydrite content reduced almost by half at about 2 hours, and then it remained approximately constant from 2 hours to 6 hours. Then it was reduced significantly between 6 and 12 hours and virtually disappeared by 24 hours.

The ettringite formed at the initial contact with water was greater than with the control mix, but its subsequent increase was relatively slow. The amount of ettringite was constant at 2% equivalent SO_4 content after 12 hours.

Table 5.1-2 shows the balance of the sulfate phases for the paste with superplasticizer. The sulfate in the original mix water was negligible, as seen in the table. The

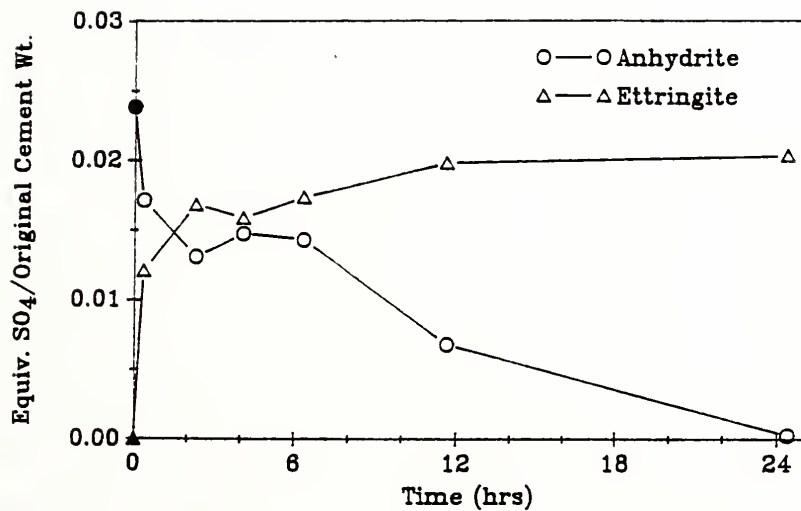


Fig. 5.1-8 Content of sulfate-bearing phases found in paste solids vs. time up to 1 day for naphthalene sulfonate bearing pastes (WB0)
(Percentage of each solid phase re-expressed in terms of its SO₄ content.)

Table 5.1-2 Total balance of sulfate-bearing phase for mix WB0

(Percentages expressed in terms of equivalent SO_4 content)

Age (hr)	Anhydrite (%)	Ettringite (%)	Σ Solid (%)	Solution (%)	Total (%)
0.00	2.47	0.0	2.47	0.01	2.48
0.37	1.71	1.21	2.91	0.02	2.93
2.33	1.31	1.68	2.99	0.01	3.00
4.12	1.48	1.59	3.06	0.01	3.07
6.37	1.43	1.73	3.17	0.02	3.19
11.67	0.68	1.98	2.66	-	-
24.37	0.03	2.04	2.06	0.01	2.07

sum of the sulfates in the solids plus the sulfate ion in the pore solution was found to be 2.9% at the first measurement. It increased slightly to 3.2% by 6 hours, and then decreased by 24 hours. This overall change in the total sulfates detected is similar to the pattern found for the control pastes.

5.2 Effects of Alkalies on Naphthalene Sulfonate Superplasticizer Absorption on White Cement W

In this section, experimental results of the mix series coded WAX and WBX are covered. The WAX series mixes were designed first to examine the effect of the alkali hydroxide in the mix water on the adsorption of naphthalene sulfonate superplasticizer for the white cement W. Using a 2% dosage of superplasticizer A, different amounts of KOH were dissolved in the mix water. The dosages used were 0.3%, 0.45%, 0.6%, 0.9%, and 1.2%, expressed as equivalent Na_2O content in the cement. The individual mixes were coded as mix WA0 (for the control without KOH addition), and WA1, WA2, WA3, WA4, and WA5, respectively. The removal of the admixture from solution prior to set was monitored.

Then a series of mixes coded WBX was prepared. This series was designed to investigate the effect of different alkali salts on the removal of naphthalene sulfonate superplasticizer from the cement paste solution. A constant 1.55% dosage of superplasticizer B was used. In this series, KOH, K_2SO_4 , and Na_2SO_4 were added to the mix water in amounts equivalent to 0.6% Na_2O in the cement. These mixes were coded WB3, WBK, and WBN, respectively. The control mix for this series was WB0,

results for which have been previously described.

5.2.1 Effects of KOH Addition to Paste with Superplasticizer A (Mix Series WAX): Solution Phase Analysis

5.2.1.1 Removal of Superplasticizer from Solution and Physical Characteristics of Pastes

Fig. 5.2-1 shows the concentration of the naphthalene sulfonate superplasticizer A remaining in solution as a function of time for the pastes of the white cement W with different amounts of KOH addition. The dosage of the superplasticizer A was 2% by weight of cement for all pastes. However, the initial concentration of naphthalene sulfonate in the mix water was only 34 g/L, equivalent to only 1.7% by weight of cement in the mix water; the sodium sulfate impurity of the admixture referred in Chapter 3 was subtracted from the gross solid weight.

For the paste without KOH addition (WA0), a little more than a half of the superplasticizer was removed from solution (i.e. taken up by the hydrating cement) in the first 10 minutes. The concentration then remained almost constant thereafter. The rheological condition of the paste was such that the paste was watery and it segregated internally so that the larger particles formed a segregated layer at the bottom, with much bleeding evident at the top. This segregation was obviously due to the heavy dosage of superplasticizer.

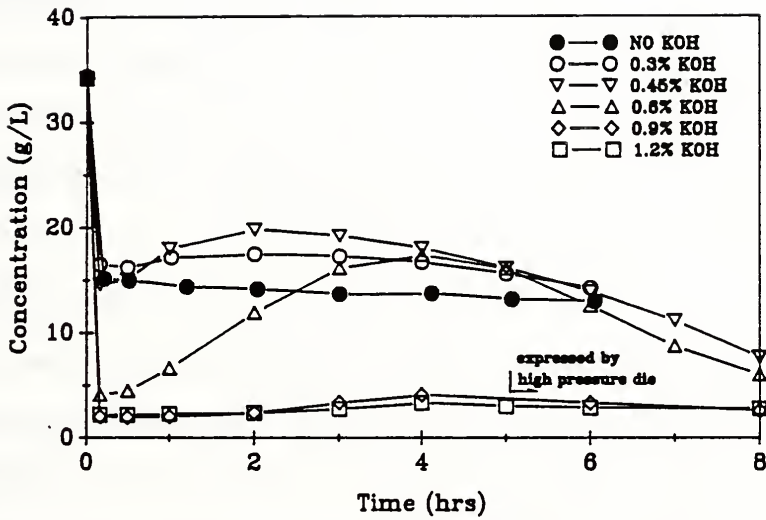


Fig. 5.2-1 Concentration of residual superplasticizer A in mix water and pore solution vs. time for pastes W with different KOH addition (WAX)

It has been shown previously (Section 5.1.1) that an addition of a heavy dose of naphthalene sulfonate superplasticizer B (1.55%) resulted in an early stiffening and an almost complete removal of the admixture. Here, no such early stiffening effect was found.

For the pastes with 0.3% or 0.45% KOH additions (WA1 and WA2, respectively), the initial amounts of superplasticizer removed from solution were approximately the same as for the mix without KOH addition. However, here some of the initially removed superplasticizer was released back into the solution progressively over several hours, and then was re-absorbed. This phenomenon was more significant as the level of the KOH addition increased. For the paste with 0.6% KOH dosage (WA3), a large portion of the admixture went through this cycle of release to the solution and then subsequent removal from solution.

The addition of KOH also changed the physical characteristics of the cement pastes. For low and intermediate dosages of KOH addition (0.3% to 0.6% Na_2O equivalent), the paste characteristics changed to more homogeneous states, and segregation and bleeding were not observed. Furthermore at such dosage levels, setting was slow enough that separation of solution for analysis would be done by filtration over the full 8 hour period covered.

For pastes with heavier dosages of KOH, i.e. 0.9% (WA4) and 1.2% (WA5), both the solution concentration responses and the overall paste physical characteristics changed. For these pastes, nearly all of the superplasticizer was removed from solu-

tion immediately, and it was never fed back to the solution. The physical characteristics of the pastes appeared to change significantly with time. Initially they were unsegregated, fluid pastes, similar to those at lower KOH dosages, but by 1 hour they had changed to stiff gels. This change was followed by progressive stiffening and early setting. By 5 hours, this solution could no longer be filtered off from the paste, and it needed to be recovered by the high pressure die method.

5.2.1.2 Inorganic Ion Concentrations in the Solution for Paste WA3

The paste with 0.6% KOH addition (WA3), which exhibited the peculiar reversible removal of the superplasticizer from solution most significantly, was selected and its pore solutions were analyzed further. Fig. 5.2-2 present the concentrations of K^+ , Na^+ , Ca^{2+} , and OH^- ions of two replicate runs on different days as functions of time. For technical reasons, the sulfate ion concentrations were not measured.

The concentrations at time zero (filled symbols) are those in the mix water prior to contact with cement, in which the superplasticizer and additional KOH were already dissolved.

The concentrations of the cations (K^+ , Na^+ , and Ca^{2+}) were found to be constant throughout the this 8-hour period of measurement. It is noticed from the figure that the OH^- ion concentration in solution decreased progressively for the first 3 hours or so, and then remained approximately constant.

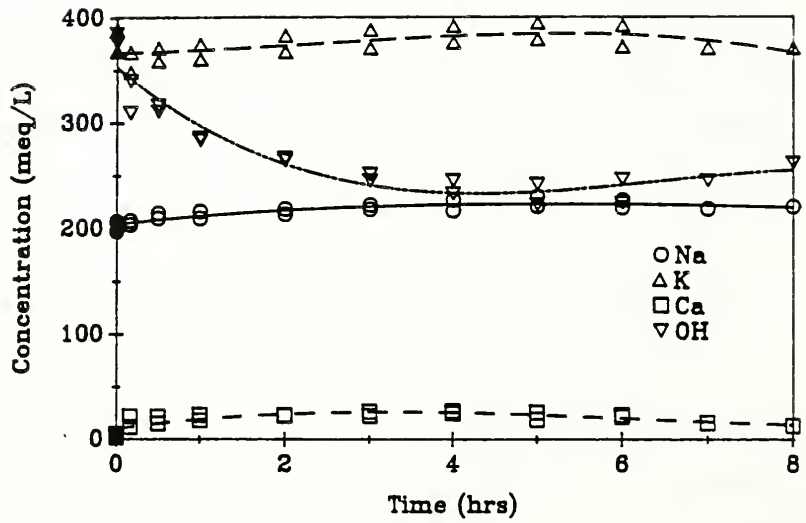


Fig. 5.2-2 Concentration of inorganic ions in mix water and pore solution vs. time in paste with 2% naphthalene sulfonate superplasticizer A and 0.6% KOH addition (WA3)

5.2.2 Effects of KOH Addition to Paste with Superplasticizer B (WB3): Solution Phase Analysis

5.2.2.1 Physical Characteristics of Paste

For comparison with the previous results, similar experiment carried out using naphthalene sulfonate superplasticizer B instead of superplasticizer A. The actual dosage of superplasticizer B used here was selected so as to exhibit the same response of UV absorbance for the long wavelength band (290 nm) of naphthalene sulfonate as the superplasticizer A did at a dosage of 2.0%, as was previously shown in Fig. 4.3-1. KOH was added at 0.6% Na_2O equivalent by weight of cement. Control paste for this series (without KOH) was WB0.

The physical characteristics of this paste with superplasticizer B and a 0.6% KOH dosage were similar in all respects to those of the corresponding paste made with superplasticizer A. The mini-slump spread values with time for this paste are plotted in Fig. 5.2-3. The fluidity is modest for the first hour, but seems to increase substantially by 2 hours to a mini-slump spread level of 500%. However, this increase in fluidity is temporary, and by 4 hours the spread was again reduced to a low value. The increase in the mini-slump value corresponds approximately to the time of release of naphthalene sulfonate superplasticizer into the solution.

The pastes behaved as uniform fluid pastes without exhibiting segregation, and setting was delayed so that separation of solution for analysis could be done by filtra-

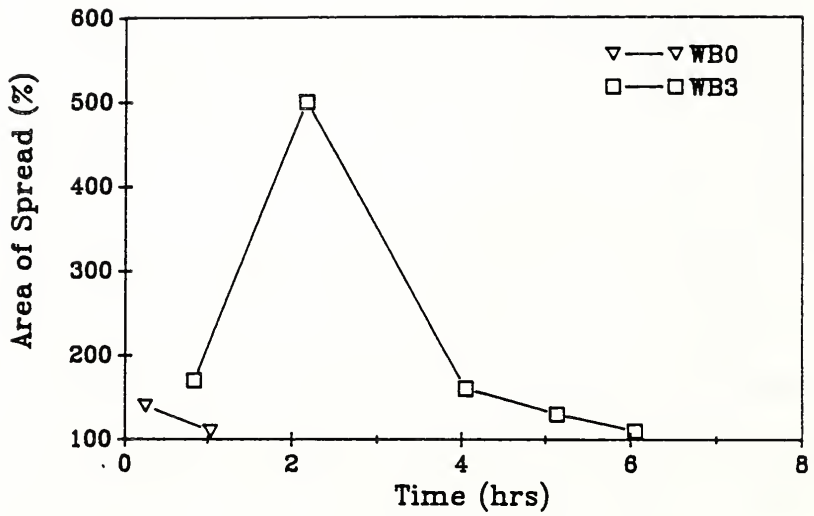


Fig. 5.2-3 Area of spread in mini-slump test vs. time for mixes WB3 and WB0

tion for the full 8-hour period covered.

5.2.2.2 Removal of Superplasticizer from Solution

Fig. 5.2-4 shows the time pattern of superplasticizer concentration in the solution of this paste (WB3), and of the two runs of the previously discussed corresponding paste with superplasticizer A (WA3). The initial absorption and the subsequent release of the naphthalene sulfonate superplasticizer B was observed to be entirely equivalent in its magnitude and duration to that seen previously in the corresponding paste with superplasticizer A. This indicates that the desorption re-adsorption phenomenon cannot be attributed to a particular brand of naphthalene sulfonate superplasticizer.

5.2.2.3 Inorganic Ion Concentrations in the Solution Phase

Fig. 5.2-5 presents the concentrations of K^+ , Na^+ , Ca^{2+} , OH^- and SO_4^{2-} ions as functions of time for the paste WB3. The SO_4^{2-} concentrations here were determined by the $BaSO_4$ gravimetric precipitation method.

It was found that the concentration of the Na^+ ion was constant at approximately 130 meq/L for the whole period. This concentration level is lower than that found with the equivalent paste with superplasticizer A. Most of the Na^+ ion is obviously derived from the superplasticizer in either case. This indicates that superplasticizer B contains less sodium than superplasticizer A, even though the UV absorption response of those

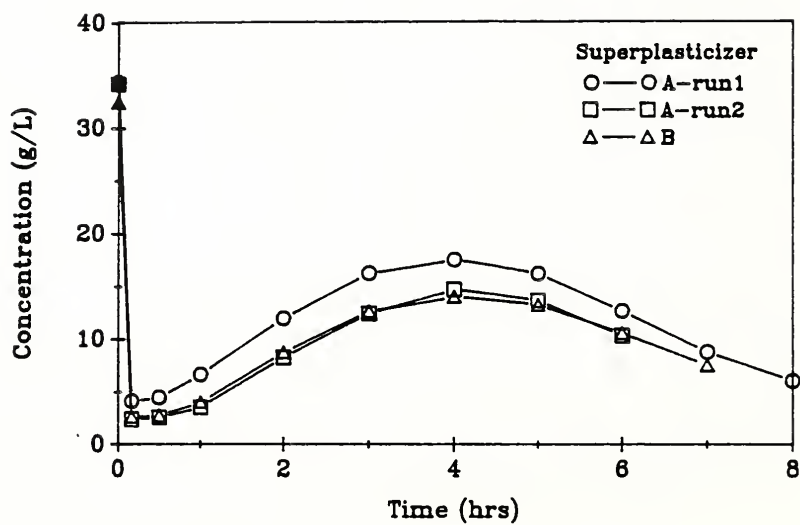


Fig. 5.2-4 Concentration of residual superplasticizer in mix water and pore solution vs. time for pastes W with naphthalene sulfonate superplasticizer A or B and 0.6% KOH addition (WA3, WB3)

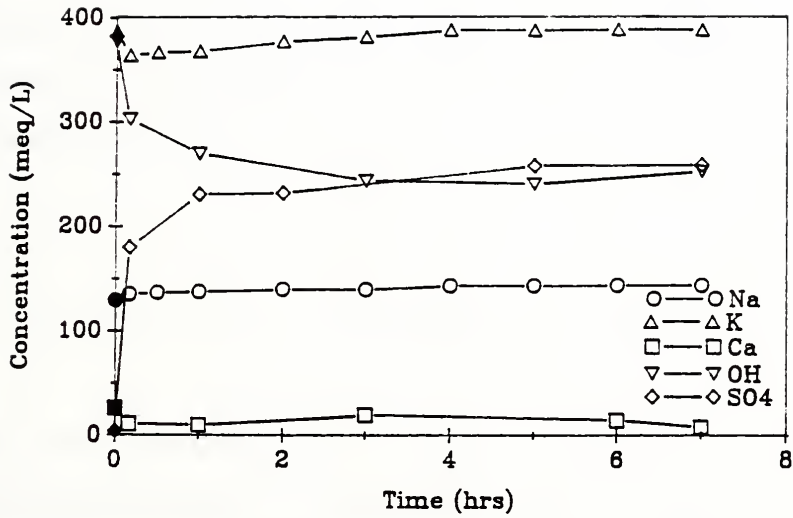


Fig. 5.2-5 Concentration of inorganic ions in mix water and pore solution vs. time in paste with 1.55% naphthalene sulfonate superplasticizer B and 0.6% KOH addition (WB3)

two superplasticizers are similar. The concentrations of the other cations (K^+ and Ca^{2+}) were constant with time, at around the same levels as those for the pastes WA3.

The SO_4^{2-} ion, which was not present in the mix water, dissolved massively into the solution phase from the cement immediately after its initial contact with water. It then stayed at around 230 meq/L for the rest of the measurement period. The OH^- ion concentration was at about 400 meq/L in the mix water, due to the added KOH. It then decreased at first, then stabilized at a level of about 230 meq/L and remained approximately constant. Aside from the difference in Na^+ ion level, the results are similar to what was previously exhibited in Fig. 5.2-2 for the corresponding paste with superplasticizer A.

5.2.3 Effects of Alkali Sulfate Addition to Paste with Superplasticizer B (WBK, WBN): Solution Phase Analysis

In this section, results are reported for pastes similar to those in Section 5.2.2 except that alkali were added as alkali sulfates (K_2SO_4 and Na_2SO_4) instead of as alkali hydroxide. Superplasticizer B was again used, and the addition level of the alkali sulfates was again 0.6% Na_2O equivalent by weight of cement. The superplasticizer addition level was again 1.55%. The paste with K_2SO_4 was coded WBK; that with sodium sulfate was coded WBN.

5.2.3.1 Physical Characteristics of the Pastes

The initial physical characteristics of both pastes WBK (with K_2SO_4) and WBN (with Na_2SO_4) were similar to each other. In contrast to pastes with a corresponding level of KOH, these pastes remained watery and exhibited a high level of segregation and bleeding, and remained so for 6 hours or more.

Fig. 5.2-6 shows the results of the mini-slump test series with time of four pastes. Paste WB0 shows the response for the control paste with this superplasticizer, but without other additions; WB3 shows the changed response with 0.6% Na_2O equivalent KOH added; and WBK and WBN show the changed responses with 0.6% Na_2O equivalent K_2SO_4 and Na_2SO_4 added, respectively. As shown previously, the superplasticized white cement paste showed initially no fluidity and was stiffened rapidly. Addition of the KOH increased the fluidity somewhat, but only temporarily.

The patterns of the the mini-slump value for the superplasticized pastes with the two alkali sulfates were basically the same. The fluidity in both cases were much higher than with KOH, with spread percentages well over 1000%. This extreme fluidity persisted for about 7 hours for the Na_2SO_4 -treated paste, 9 hours for the K_2SO_4 -treated paste. Subsequently the fluidity rapidly decreased and set occurred rapidly thereafter.

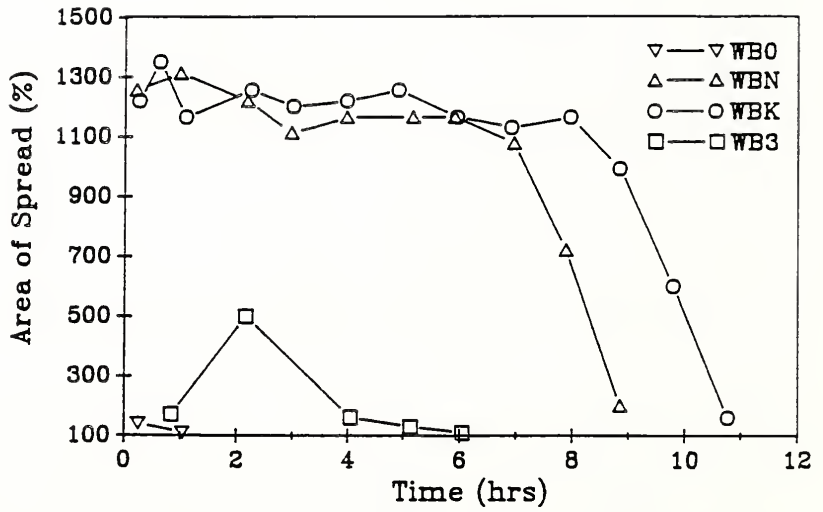


Fig. 5.2-6 Area of spread in mini-slump test vs. time for mixes WBK, WBN, WB3, and WB0

5.2.3.2 Removal of Superplasticizer from Solution

Fig. 5.2-7 shows a comparison of the residual concentrations of superplasticizer B in the paste solution as functions of time for pastes WB3, WBK, and WBN.

The pattern of removal of superplasticizer from solution was different for the KOH-treated paste than for the two alkali sulfate treated pastes. As previously noted, in the presence of the KOH, the superplasticizer was nearly completely removed initially, then some of the previously removed superplasticizer was returned to the solution after about 1 hour, and it was subsequently again removed later.

In contrast, for the alkali sulfate treated pastes, the initial removal from solution of the superplasticizer was only about one third of that for the paste with KOH. Thereafter, the superplasticizer concentration decreased gradually; the rate being a little faster for the Na_2SO_4 -treated paste. For neither paste was the phenomena of temporary return of superplasticizer to solution observed. Nevertheless, at any age, the concentration of superplasticizer remaining in solution was always much higher with the alkali sulfates than with the KOH.

5.2.3.3 Inorganic Ion Concentrations in the Solution Phase

Fig. 5.2-8 and Fig. 5.2-9 show inorganic ion concentrations as a function of time for the superplasticized pastes with K_2SO_4 and Na_2SO_4 respectively. Again the SO_4^{2-} ion concentrations were determined by the BaSO_4 gravimetric precipitation method.

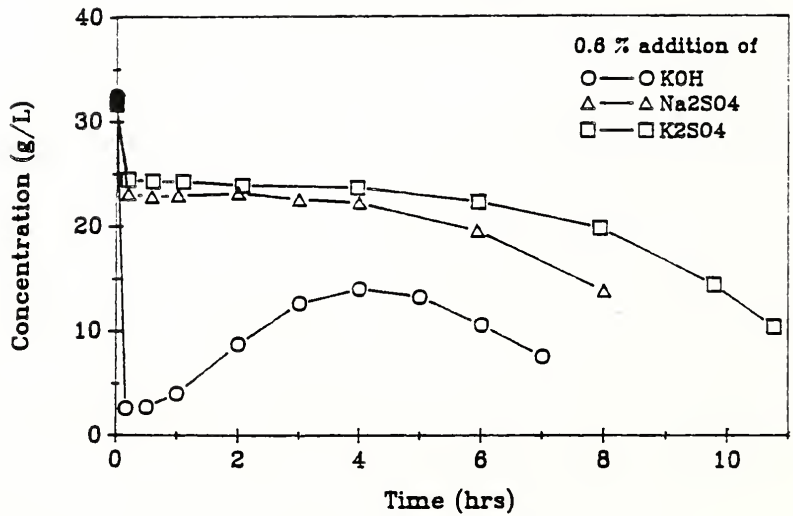


Fig. 5.2-7 Concentration of residual superplasticizer in mix water and pore solution vs. time for pastes W with naphthalene sulfonate superplasticizer B and 0.6% addition of K₂SO₄, Na₂SO₄, and KOH (WBK, WBN, WB3)

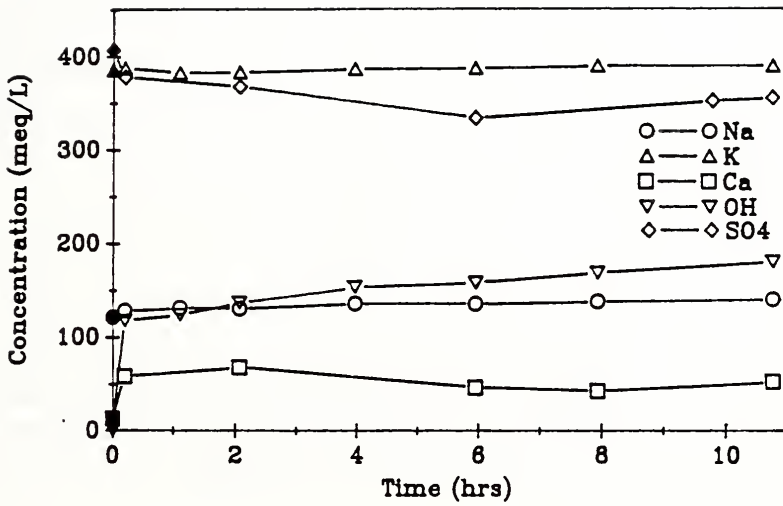


Fig. 5.2-8 Concentration of inorganic ions in mix water and pore solution vs. time in paste with 1.55% naphthalene sulfonate superplasticizer B and 0.6% K_2SO_4 addition (WBK)

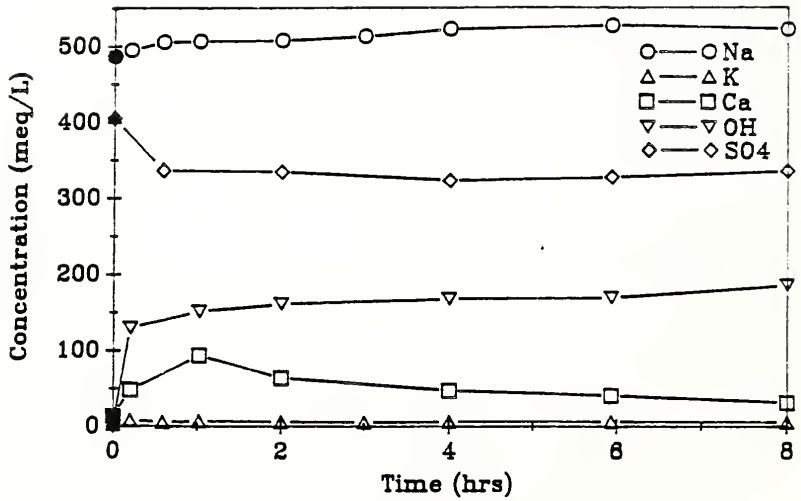


Fig. 5.2-9 Concentration of inorganic ions in mix water and pore solution vs. time in paste with 1.55% naphthalene sulfonate superplasticizer B and 0.6% Na₂SO₄ addition (WBN)

For the paste with K_2SO_4 , the cation changes were similar to those for the paste with KOH, except for the Ca^{2+} ion. The Ca^{2+} ion concentration for the paste WBK increased immediately over 50 meq/L and remained nearly constant at this level, which was significantly higher than the paste with KOH.

For the anions, the SO_4^{2-} ion concentration was initially high in the mix water and decreased only a little. The OH^- ion rose up to 130 meq/L after the initial contact then increased gradually.

Next for the paste with Na_2SO_4 (Fig. 5.2-9), the Na^+ ion remained at the highest level (about 500 meq/L) for the whole period of analysis due to its extra addition plus from the superplasticizer. There was almost no K^+ ion detected. The Ca^{2+} ion concentration rose to 90 meq/L at one hour then gradually decreased to a level around 30 meq/L, which is also higher than that for the paste WB3.

The anion patterns were quite similar to those patterns for the paste with K_2SO_4 , and both the OH^- and the SO_4^{2-} ion concentrations were stabilized at approximately the same levels as those for the paste WBK. It should be noted that in both cases the SO_4^{2-} concentration level remained high, at least during this eight-hour period.

5.3 Effects of the Sulfate and Hydroxide Ions on Removal of Superplasticizer from Solution

5.3.1 Objectives of the Experiment

The results of experiments described in the previous section raise some questions with respect to the effects of alkalis on the removal of the naphthalene sulfonate superplasticizer from solution.

First, the study on the effects of alkali hydroxide on superplasticizer A showed that initial removal of the superplasticizer from solution increased with increasing dosage of KOH. In addition, the rheological behavior changed with increasing additions of KOH.

It was noticed that the removal pattern of the superplasticizer for the paste WB0 shown in Fig. 5.1-6, was significantly different from that of the paste WA0 shown in Fig. 5.2-1, although both are control pastes of the same cement without alkali addition. Superplasticizer B was almost completely removed from solution in the first 16 minutes, but an initial removal of superplasticizer A was only about half the amount added. Table 5.3-1 shows the inorganic ion concentration in the mix waters of pastes WA0 and WB0 as analyzed by atomic absorption and ion chromatography. The results indicate that superplasticizer A contains significantly more Na_2SO_4 impurity than the superplasticizer B; the corresponding SO_4^{2-} ion concentrations in the mix water were about 27 meq/L and 5 meq/L respectively. Actually, the total ionic con-

Table 5.3-1 Concentrations of inorganic ions and superplasticizer in the mix water for the paste WA0, WB0, WBN0

Mix Code	WA0	WB0	WBN0
Superplasticizer (g/L)	34.0	31.8	31.8
Inorganic composition (by analysis) (meq/L):			
Na ⁺	201.0	116.1	120.3
K ⁺	0.0	0.9	0.0
Ca ²⁺	3.4	11.6	10.5
OH ⁻	0	0	0
SO ₄ ²⁻	26.5	4.5	25.0

centrations of the solution of cement W without superplasticizer is so small that even a modest difference in the amount of SO_4^{2-} added in the mix water may affect the removal of superplasticizer from the solution considerably.

In order to further investigate the effects of the anions concerning the points mentioned above, three more superplasticized paste mixes were examined in a supplemental study. All three pastes were dosed with 1.55% naphthalene sulfonate superplasticizer B. The first is a repeat of the paste mix WB3, i.e. water:cement ratio 0.5 white cement with the superplasticizer and incorporating a 0.6% KOH addition. This paste is coded WB3'. The second paste was a similar white cement paste with 1.2% KOH added in the mix water, coded WB5. This paste is comparable to WA5, previously described. Third mix is a similar white cement paste with 0.03% Na_2SO_4 addition in the mix water, coded WBN0. This amount of Na_2SO_4 is equal to the sulfate impurity of superplasticizer A, as was shown in Table 5.2-1. For these three pastes, the residual superplasticizer concentration in solution, the OH^- ion concentration, the SO_4^{2-} ion concentration, and the CaSO_4 bearing phases of the solids were analyzed as functions of time until the time of set.

5.3.2 Effects of KOH and Sulfate Additions on Residual Concentration of Superplasticizer B, on Anion Concentrations, and on Solid Phases Present

5.3.2.1 Removal of Superplasticizer from Solution

Fig. 5.3-1 shows the remaining concentration of superplasticizer in solution as a function of time for the pastes WBN0, WB3', and WB5. The pattern for the paste without any alkali addition, previously examined as the mix WB0, is also presented in the figure for reference.

For the paste with a small amount of Na_2SO_4 added (WBN0), the removal of superplasticizer from solution immediately after the contact with water was reduced to about half of the initial concentration, in contrast to the almost complete removal for the paste WB0. The subsequent decrease in concentration was small. Paste WBN0 was found to be extremely fluid and it exhibited extreme segregation and bleeding, similar to the behavior of paste WA0, but quite different from that of paste WB0. It should be recalled that the latter was stiff, exhibited no segregation or bleeding.

For the paste with 0.6% KOH addition (WB3'), the pattern of the initial removal and the subsequent "desorption" of the superplasticizer previously reported for paste WB3 was repeated. However, for this mix, the amount of superplasticizer released back to solution was a little smaller than for the previous paste WB3.

For the paste with 1.2% KOH addition (WB5), almost all the superplasticizer was removed from solution within 10 minutes and there was no subsequent "desorption" of

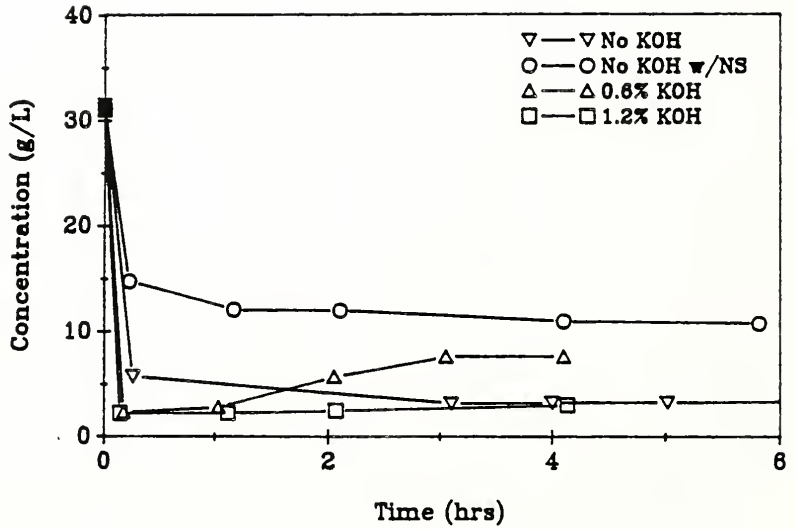


Fig. 5.3-1 Concentration of residual superplasticizer in mix water and pore solution vs. time for pastes W with naphthalene sulfonate superplasticizer B (WB0) and with 0.03% addition of Na_2SO_4 , 0.6%, and 1.2% addition of KOH (WBN0, WB3', WB5)

superplasticizer observed. This adsorption pattern is the same as that previously seen with paste WA5. The present paste was found to stiffen actually within 6 minutes. However, there was a noticeable difference in this stiffening from the rapid solidification previously observed for the paste WB0. Here the cement particles seemed to be flocculated and small aggregations were found during the first 6 minutes while the paste was still fluid. For the previous paste without KOH (WB0), the cement particles had remained well dispersed in the fluid mass.

5.3.2.2 Anion Concentrations in the Solution Phase

Fig. 5.3-2 summarizes the SO_4^{2-} ion concentrations of the three pastes vs. time. The pattern for the paste WB0 is also shown in the same figure. The SO_4^{2-} ion concentrations were determined here by ion chromatography. By comparing the patterns for pastes WB0, WB3', and WB5, it is evident that the initial dissolution of the sulfate was greater as the alkalinity of the mix water increased. The sulfate ion concentrations for the pastes WB3' and WB5 increased rapidly at first, and then more slowly. For the paste WBN0, there was a small peak in the sulfate concentration to about 50 meq/L at 10 minutes, but it decreased again and stayed around the level of 30 meq/L for the rest of the period.

Fig. 5.3-3 exhibits the OH^- ion concentration of the three pastes and the paste WB0 as functions of time. For the paste WBN0, the mix water did not contain any hydroxide ion; the OH^- concentration of the paste increased to about the same concentration as that of paste WB0 (90 meq/L) in the first 14 minutes. It did not change

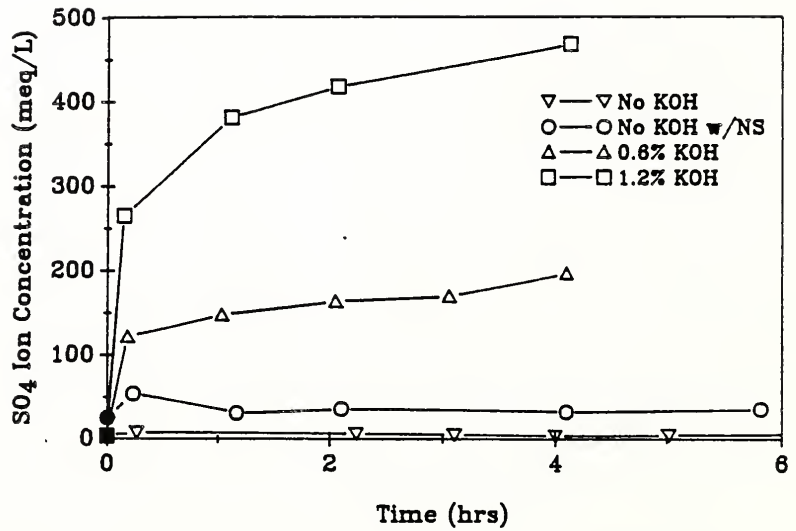


Fig. 5.3-2 Concentration of the SO_4^{2-} ion in mix water and pore solution vs. time for pastes W with naphthalene sulfonate superplasticizer B (WB0) and with 0.03% addition of Na_2SO_4 , 0.6%, and 1.2% addition of KOH (WBN0, WB3', WB5)

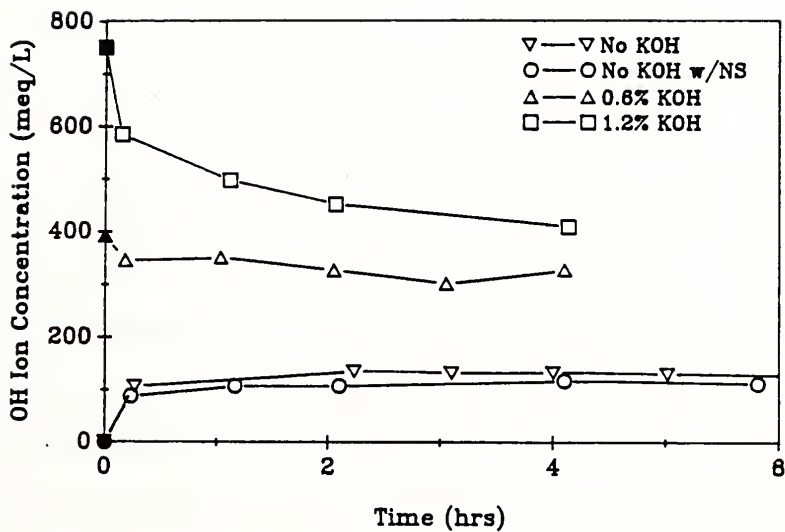


Fig. 5.3-3 Concentration of the OH^- ion in mix water and pore solution vs. time for pastes W with naphthalene sulfonate superplasticizer B (WB0) and with 0.03% addition of Na_2SO_4 , 0.6%, and 1.2% addition of KOH (WBN0, WB3', WB5)

thereafter.

For the pastes WB3' and WB5, the initial high concentrations of the OH^- ion in the mix water were not maintained in the pastes. Rather they decreased progressively as hydration proceeded. This decrease was mainly a response to the rapid increases in the SO_4^{2-} ion concentration by dissolution of the anhydrite. The net result was that the excess of the Na^+ ions released from the superplasticizer was here balanced by increase in the SO_4^{2-} ion concentration, rather than by increase in OH^- ion concentration.

5.3.2.3 Solid Phase Analyses

The CaSO_4 -bearing phases observed in the solids separated from these three pastes were insoluble anhydrite and ettringite only, as were the cases for the pastes WO and WB0. Fig. 5.3-4 shows the changes of anhydrite contents (expressed as equivalent SO_4 content) as functions of time for the three pastes and the paste WB0. For the paste WBN0, the decrease of the anhydrite within the first 14 minutes was almost the same as that for the paste WB0. Subsequently the anhydrite content remained almost constant, before again starting a progressive decline at about 2 hours. The anhydrite content of paste WB0 did not show an early constant period; however, it did remain approximately constant after 2 hours.

The patterns for the paste WB3' and WB5 were similar to each other, but very different from those described above. The anhydrite content declined immediately to

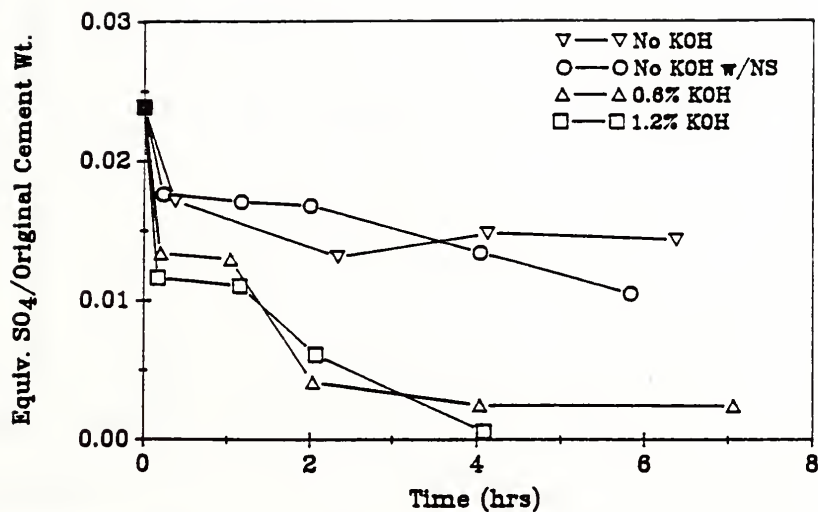


Fig. 5.3-4 Content of anhydrite in paste solids vs. time for pastes W with naphthalene sulfonate superplasticizer B (WB0) and with 0.03% addition of Na_2SO_4 , 0.6%, and 1.2% addition of KOH (WB0, WB3', WB5) (Percentage of anhydrite re-expressed in terms of its SO_4 content.)

around 1.2% equivalent SO_4^{2-} ; it then continued to decline rapidly for both paste: reaching essentially zero at 4 hours for the paste with 1.2% KOH addition.

Fig. 5.3-5 shows the ettringite content in the separated solid vs. time for the same three pastes and the paste WB0. Although the paste WBN0 is identical to the paste WB0 except for the small addition of Na_2SO_4 , the amount of the ettringite formed in the first 10 minutes was cut in half, from 1.2% to 0.6% equivalent SO_4 . This significant difference in the ettringite produced was maintained with age over the period investigated. It is thus considered that this difference in the ettringite formation may have contributed to the different rheological behaviors of two pastes.

For the paste WB3', the initial ettringite formation at 10 minutes was around 1% but it rose to 1.6% at 1 hour and continued to increase to higher levels at a given age than did the paste WB0.

An unusual response was found for the paste WB5. No ettringite had formed for almost the first 2 hours of the hydration period; thereafter, ettringite started to form, and the amount present increased fairly rapidly. This paste was stiffened quickly, within 15 minutes; subsequently it remained in a gelatinous condition until it set.

Table 5.3-2 shows the balance of the SO_4 -bearing phases in pastes WBN0, WB3', and WB5.

For paste WBN0, the sum of the sulfates allocated in the solids plus the SO_4^{2-} ion in the pore solution remained essentially constant for the 2 hours, then decreased slightly. It should be recalled that the corresponding total percentages for the control

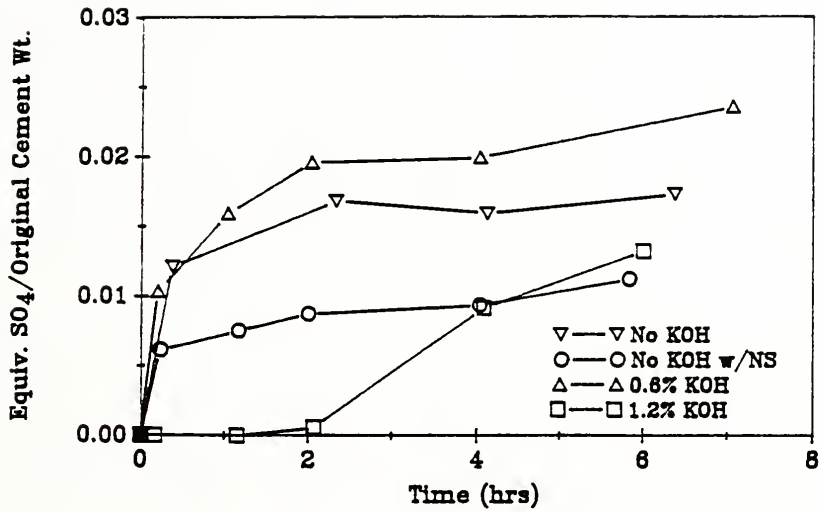


Fig. 5.3-5 Content of ettringite in paste solids vs. time for pastes W with naphthalene sulfonate superplasticizer B (WB0) and with 0.03% addition of Na_2SO_4 , 0.6%, and 1.2% addition of KOH (WBN0, WB3', WB5) (Percentage of ettringite re-expressed in terms of its SO_4 content.)

Table 5.3-2 Total balance of sulfate-bearing phase for mix WBN0, WB3', and WB5

(Percentages expressed in terms of equivalent SO_4 content)

Mix #	Age (hr)	Anhydrite (%)	Ettringite (%)	Σ Solid (%)	Solution (%)	Total (%)
WBN0	0.00	2.47	0.00	2.47	0.06	2.53
	0.23	1.76	0.62	2.37	0.13	2.50
	1.17	1.71	0.75	2.46	0.07	2.53
	2.00	1.68	0.87	2.55	0.09	2.64
	4.03	1.34	0.94	2.28	0.08	2.35
	5.83	1.04	1.12	2.17	0.09	2.25
WB3'	0.00	2.47	0.00	2.47	0.01	2.48
	0.20	1.33	1.03	2.37	0.29	2.66
	1.03	1.29	1.59	2.88	0.35	3.24
	2.03	0.41	1.96	2.37	0.39	2.76
	4.03	0.24	1.99	2.24	0.47	2.71
	7.07	0.24	2.36	2.60	-	-
WB5	0.00	2.47	0.00	2.47	0.01	2.48
	0.17	1.16	0.00	1.16	0.64	1.79
	1.15	1.10	0.00	1.10	0.91	2.02
	2.07	0.61	0.06	0.67	1.00	1.67
	4.08	0.06	0.91	0.97	1.12	2.10
	6.00	0.00	1.32	1.32	-	-

* The total SO_4 content of the cement, separately determined, was 3.76% as SO_4 .

mix with superplasticizer free from sulfate impurity (WB0) were generally higher, increasing to around 3.0% by 6 hours (Table 5.1-2).

For paste WB3', the sum of the sulfates in the solids and the sulfate ions increased significantly to 3.2% for the first 1 hour, and then declined to around 2.7% by 4 hours. These total percentages were higher than those for the previous paste WBN0.

In contrast to these effects, the total sulfates accounted for in paste WB5 decreased at the first measurement to 1.8%, the decrease reflecting obvious dissolution of anhydrite without precipitation of identifiable ettringite. It then fluctuated in a range between 1.7% and 2.1%, lower total allocated sulfate contents than for any other mix of WBX series. The decrease in the total sulfates in the solids for the first 2 hours was larger than the increase in the sulfate ion concentration.

5.4 Discussion

5.4.1 Analyses for Control and Superplasticized White Cement Pastes (WO and WB0)

In the control paste, ettringite formation at early ages was moderate, probably because the rate of dissolution of insoluble anhydrite was slow. Considering that the anhydrite content was continuously reduced during the first 6 hours, it appears that the rate of anhydrite dissolution controls the rate of ettringite formation.

When the superplasticizer was added, the initial formation of ettringite and the consumption of insoluble anhydrite were both accelerated by the presence of the

superplasticizer. Both phenomena occurred probably because the cement particles were more dispersed by the action of the superplasticizer during the first 20 minutes of hydration. In solution, both the calcium ion and the sulfate ion were low from the early stage of hydration, probably as a result of the intense ettringite formation.

The peculiar quick stiffening of paste WB0, which was not a false set, can be attributed to the intense ettringite formation and the almost complete removal of the superplasticizer in the early stages of hydration. The ettringite content reached as high as 1.7% of SO_4 equivalent by 1 hour. This ettringite formation itself could cause filling and bridging the interparticle spaces, and lead to a quick setting of the paste. It is believed that the superplasticizer was preferentially incorporated with this ettringite, and was removed from the solution during the first 20 minutes of hydration. Thus the solution phase lacking residual superplasticizer, did not have any potential of dispersing the solid particles; this also appeared to assist this quick setting.

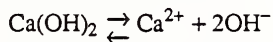
5.4.2 Effects of the OH^- ion on Hydration of Cement W and on Removal of Superplasticizer from Solution

From the results of the pastes with superplasticizer A and additional KOH (the WAX pastes), it appears that the higher hydroxide ion concentration in the mix water promoted the initial removal of the naphthalene sulfonate from the paste solution as shown in Fig. 5.2-1. But the picture is not simple. Based on the rheological feature of the pastes and the results of calcium sulfate phase analysis for analyses of WBX series, the early hydration pattern of the white cement W seems to be altered both by

mix water with dissolved alkali hydroxide, and by the action of the superplasticizer.

The form of the calcium sulfate in the white cement W is entirely composed of "insoluble" anhydrite. A higher OH^- concentration in the original mix water accelerates the rate of anhydrite dissolution. This results in a faster depletion of the anhydrite, and increases of the SO_4^{2-} ion concentration in solution. This increased dissolution of calcium sulfate releases an equivalent additional amount of the Ca^{2+} ion into the solution.

The effect of the OH^- ion was evident in the extreme case of a large addition of KOH in the mix water. For the paste WB5, although the SO_4^{2-} ion concentration in pore solution was markedly high, ettringite was not formed at all for the first 2 hours. Nevertheless the paste was stiffened within 15 minutes. In solutions of higher alkalinity than that of saturated $\text{Ca}(\text{OH})_2$ solution, the equilibrium



shifts strongly to the precipitation side and the amount of $\text{Ca}(\text{OH})_2$ remaining dissolved in solution is reduced. It would seem that in the presence of high OH^- ion concentrations, the calcium sulfate would tend to dissolve rapidly to make up the "shortage" of Ca^{2+} ions. As more calcium sulfate is dissolved, the Ca^{2+} ions are progressively incorporated in additional $\text{Ca}(\text{OH})_2$ but the SO_4^{2-} ions remain in solution. In the WB5 paste, a prompt $\text{Ca}(\text{OH})_2$ precipitation occurred and may have caused the quick set. The loss on ignition data for the paste WB5 was as high as 3.01% at 10 minutes, and 3.22% at 1 hour, compatible with the existence of a large content of calcium hydroxide. The same pastes had very low evaporable water contents, as low as

0.38% and 0.55% at 10 minutes and 1 hour, respectively, so a large amount of cement hydration had not taken place.

The lack of ettringite formation may be explained by the possibility that the rate of the Ca(OH)_2 precipitation is so fast that the calcium ion selectively precipitates as calcium hydroxide in this high pH solution. As hydration continues, the increase of the SO_4^{2-} ion concentration and the calcium ion consumption might reduce the OH^- ion concentration and slow down the rate of Ca(OH)_2 precipitation. When the OH^- ion concentration is reduced to around 0.45 N, i.e. after 2 hours of hydration, the rate of ettringite formation becomes relatively fast. It can be hypothesized that ettringite formation is hindered in solutions of OH^- ion concentrations higher than around 0.5N.

Thus for the paste WB5, a combination of the rapid precipitation of Ca(OH)_2 and the almost complete removal of superplasticizer from solution within 10 minutes was responsible for this quick set. However, this may be only applicable to this white cement because of its peculiar properties. The superplasticizer removal from solution is obviously related to this Ca(OH)_2 precipitation, but the crystals of calcium hydroxide rarely incorporate foreign organic species; the mechanism is not clear.

For the paste WB3, the superplasticized pastes with KOH added to the mix water at 0.6% Na_2O equivalent by weight of cement, this rapid Ca(OH)_2 formation seemed to occur to a limited degree only. The removal of the superplasticizer from solution might thus be due to the incorporation by poorly-crystalline ettringite. The formation of ettringite was not limited in this paste of lower OH^- ion concentration; the percen-

tage formed in the first 10 minutes was as high as 1.0% SO_4 equivalent in the solids and increased thereafter to a larger percentage than in the paste WB0.

For the pastes without the OH^- ion addition (WB0 and WBN0), the initial superplasticizer uptake and the hydration behavior are more influenced by other factors, as will be discussed later.

Thus, it appears that the early removal of superplasticizer from solution may involve different uptake mechanisms, depending on any addition made to the mix water. Most of the superplasticizer is immediately taken up by the solids in the absence of any such addition, and also in the presence of a high dosage of added KOH, but the two responses are different in cause and character. Again, it is partially due to the peculiar properties of the white cement.

Finally, it was noticed that in the mix water containing naphthalene sulfonate superplasticizer and the 0.6%, 0.9%, and 1.2% KOH treatments, a fine white precipitate was observed. A similar white precipitation was reported to develop in melamine sulfonate superplasticizer when concentrated alkali hydroxide solution was added, in research by Yilmaz et al. [76]. They considered the precipitate to be the result of "denaturation" of the admixture in such solution. However, in the present paste, the UV adsorption spectra of naphthalene sulfonate superplasticizer in the solutions with the white precipitate was identical to that of the original superplasticizer. Thus it does not appear that the plasticizing action would be affected by the response to the addition of the alkali hydroxide.

5.4.3 Effects of Sulfate Ions on Removal of Superplasticizer From Solution

Effects of the sulfate ions dissolved in the mix water on the initial adsorption of naphthalene sulfonate superplasticizer are reasonably apparent. Fig. 5.4-1 compares the time-dependent changes of the superplasticizer concentration remaining in solution for the pastes of the white cement W with different concentrations of the sulfate ion in the mix water. These pastes are WB0, WA0, WBN0, WBK, and WBN. The mix water of pastes WB0 contained 5 meq/L of the SO_4^{2-} ion, those of the pastes WA0 and WBN0 contained around 25 meq/L, and those of pastes WBN and WBK contained around 400 meq/L. It is seen that the superplasticizer concentration remains approximately constant with time for each of these pastes, but that the actual concentration levels vary considerably.

Fig. 5.4-2 shows the time-dependent changes of the SO_4^{2-} ion for the same pastes. The results of Fig. 5.4-2 indicate that the level of SO_4^{2-} retained in solution are approximately 0, 40, 330, and 360 meq/L for pastes WB0, WBN0, WBN, and WBK, respectively. These levels are approximately proportional to the dosage of SO_4 added in the mix water, but for the pastes with the higher SO_4 addition (WBN and WBK) the concentration level maintained in the cement paste solution was actually a little less than was originally present in the mix water.

It is clearly seen that the higher concentrations of sulfate ions in the mix water somewhat hinder the initial uptake of the naphthalene sulfonate superplasticizer. Judged from the results for the pastes WBK and WBN, little difference occurs

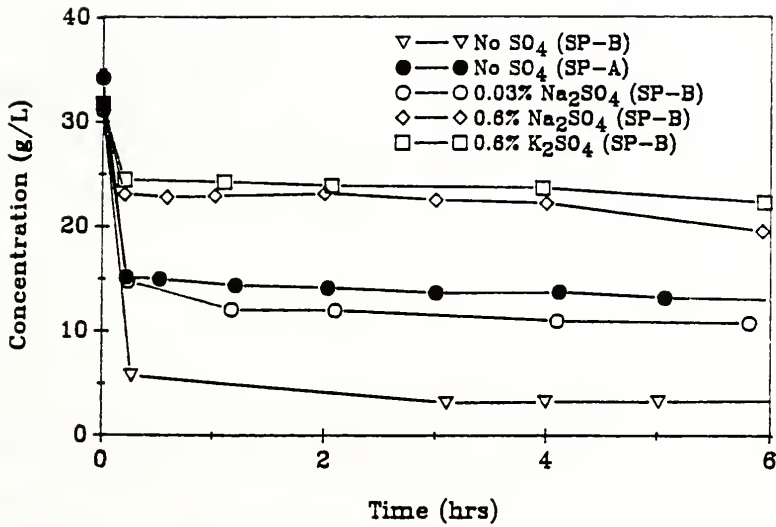


Fig. 5.4-1 Concentration of residual superplasticizer in mix water and pore solution vs. time for pastes W with naphthalene sulfonate superplasticizer A, and B (WA0, WB0), and pastes W with superplasticizer B and 0.03%, 0.6% addition of Na_2SO_4 , and 0.6% addition of K_2SO_4 (WBN0, WBN, WBK)

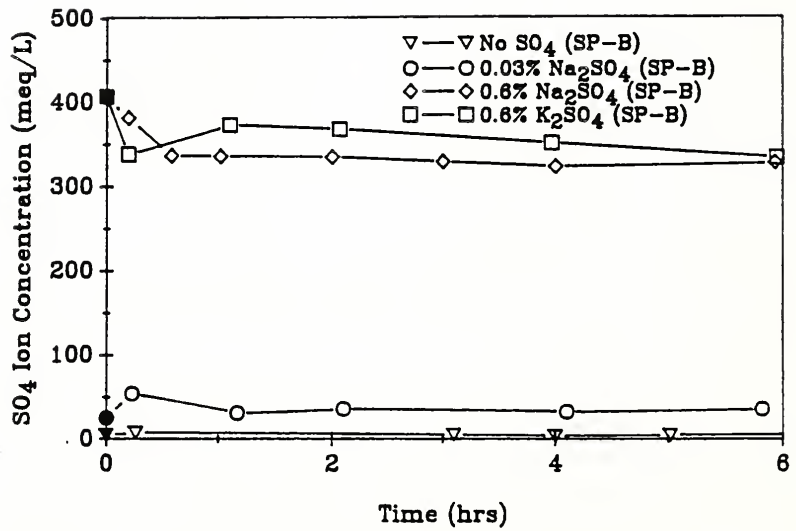


Fig. 5.4-2 Concentration of the SO_4^{2-} ion in mix water and pore solution vs. time for pastes WB0, WBN0, WBN, and WBK

between effects of sodium and potassium as the cation of the alkali sulfate on the adsorption characteristics of the superplasticizer.

The pastes WA0, WBN0, WBK, and WBN were all fluidized well, and the residual naphthalene sulfonate concentration in the paste solutions stayed high. Again, it is found that the residual concentration of the superplasticizer is strongly associated with the physical characteristics of the pastes. In addition, well-fluidized pastes appeared to show retardation in hydration compared to the control paste WO.

The patterns of superplasticizer adsorption of paste WA0 and WBN0 were almost identical, and the rheology of the two pastes were also similar to each other, but different from that for the paste WB0. The difference of two superplasticizers A and B in initial absorption behavior are probably explained by the amount of the sodium sulfate impurity.

The polymer anion of the naphthalene sulfonate superplasticizer and the SO_4^{2-} ion both have negative charges. Both may tend to be absorbed by positively charged surfaces of early C_3A hydration products, or incorporated into such products, almost immediately after the beginning of hydration. The white cement W has a very low alkali sulfate content; the sulfate present appears to be in the form only of anhydrite. Because of the low rate of dissolution of anhydrite, the sulfate ion concentration that is derived quickly from the cement itself is also low, as seen for the control paste WO. In this low range of sulfate ion concentration of the paste solution at very early ages, even a small amount of dissolved sulfate "impurity" apparently causes significant

interference with the removal of naphthalene sulfonate from solution.

However, this system of white cement paste W plus naphthalene sulfonate superplasticizer was so sensitive that its hydration behavior can be significantly affected by its mixing procedure. The author found that the small hand mixed specimen of WB0 remained well dispersed and showed bleeding for hours exactly like the paste WBN0. when the hand mixed WB0 paste was mixed in such a way that the mix water wet the cement slowly. The comparison hand mixed WB0 paste exhibited the quick set response usually seen for WB0 pastes when mixed vigorously in a short time.

The difference in early hydration behaviors of these superplasticized pastes with paste solutions of few sulfate ions present, are also observed in the amount of ettringite formed. Early ettringite formation (10 minutes) for the paste WB0 was 1.2% and that for the paste WBN0 was only 0.6% equivalent of SO_4 content. This difference can be partially attributable to the sulfate ion concentrations in the solution phase.

The initial removal of superplasticizer from solution was about nearly complete for paste WB0, and only about a half for paste WBN0. Consequently, the paste WB0 exhibited a peculiar quick stiffening. In contrast, WBN0 paste was completely dispersed and showed extensive bleeding for several hours. It is considered that ettringite formation itself can absorb and incorporate the naphthalene sulfonate.

For this particular white cement, the presence of naphthalene sulfonate admixture coupled with the lack of the sulfate ion in the paste solution at very early ages frequently resulted in quick premature stiffening. Adding sulfate ions along with the

superplasticizer seems to prevent this peculiar early hydration behavior. If sulfate ions are added, the amount of ettringite formed immediately is reduced, and the amount of naphthalene sulfonate superplasticizer removed from solution is also reduced; in consequence, a well-fluidized paste is produced. A possible explanation is that the initial hydration products contain more SO_4^{2-} ions and fewer absorbed superplasticizer molecules. It may be that these initial products develop a less reactive surface for ettringite crystal growth, or that they act as a kind of the coating layer. In either case, the amount of ettringite formed quickly is reduced. This response may be specific to this white cement whose gypsum is entirely in the form of slowly-dissolving anhydrite.

5.4.4 Mechanism of "Desorption" of Superplasticizer

For the superplasticized pastes with 0.6% KOH addition (WB3), the phenomenon of the temporary release of the polymer previously removed from solution was observed.

In some circumstances, the naphthalene sulfonate superplasticizer is probably incorporated unstably with the amorphous early hydration products. Thus the changes in the ionic concentrations in the paste solution could cause "desorption" of these polymers from the solid surfaces.

With melamine sulfonate superplasticizer, Yilmaz et al. [76] considered that the "adsorption" of superplasticizer at early stage of hydration is controlled by ettringite or its precursor, and that the desorption of admixture occurs as this amorphous

precursor crystallizes to ettringite. However, no actual evidence to relate the crystallinity of ettringite and the superplasticizer adsorption was given in this paper.

5.4.5 Solid Phases

From the solid phase analyses, no crystallization of gypsum from anhydrite was detected regardless of the presence of the superplasticizer, or the concentration of the SO_4^{2-} or the OH^- ions in solution.

The paste systems to which the alkali hydroxide was intentionally added preserve a high OH^- ion concentration in the pore solution, which increases the solubility of calcium sulfates in general, thus hindering the formation of any hydrous calcium sulfate phases. As long as the OH^- ion concentration is high, gypsum is not able to form even in the presence of some sulfate ions.

For the normal pastes without an addition of KOH, the absence of gypsum or hemihydrate phases is probably explained by the fact that in the actual absence of alkali sulfates, the slow rate of dissolution of anhydrite keeps the CaSO_4 level in solution below the saturation level. In addition, the ettringite formation process constantly consumes the sulfate ion from the liquid phase. Therefore it is not unexpected to observe such direct conversion to ettringite without a transient state of gypsum, when the initial form of calcium sulfate in cement is insoluble anhydrite.

5.5 Effects of Melamine Sulfonate Superplasticizer on White Cement "W" Pastes : Physical Characteristics of Pastes and Removal of Superplasticizer from Solution

In the course of this research program, the study on white cement paste with melamine sulfonate superplasticizer was carried out to a limited extent. The results of the preliminary experiment are reported here for reference. The paste examined was a plain mix of white cement W with 2% dosage of melamine sulfonate superplasticizer B by weight of cement. The superplasticizer was dissolved in the mix water, and no inorganic ion was added to it.

— Physical Characteristics of the Paste

The physical characteristics of the paste was peculiar, and it had not been similarly observed in any pastes of the white cement with naphthalene sulfonate superplasticizers. The hydration of the paste was very severely retarded due to the heavy dosage of the melamine sulfonate superplasticizer. The paste had been watery, and completely segregated for 2 days.

Fig. 5.5-1 shows the mini-slump spread values with time for this paste. The heavy dosage of the melamine sulfonate superplasticizer produced a entirely fluidized state (mini-slump value of over 1000%) for the first 3 hours. Then the spread value declined to 800% by 6 hours, however, it decreased only to 700% during the subsequent 18 hours. By 45 hours, the mini-slump value was dropped to 280%, and the paste was solidified several hours later. The initial set was at 54 hours.

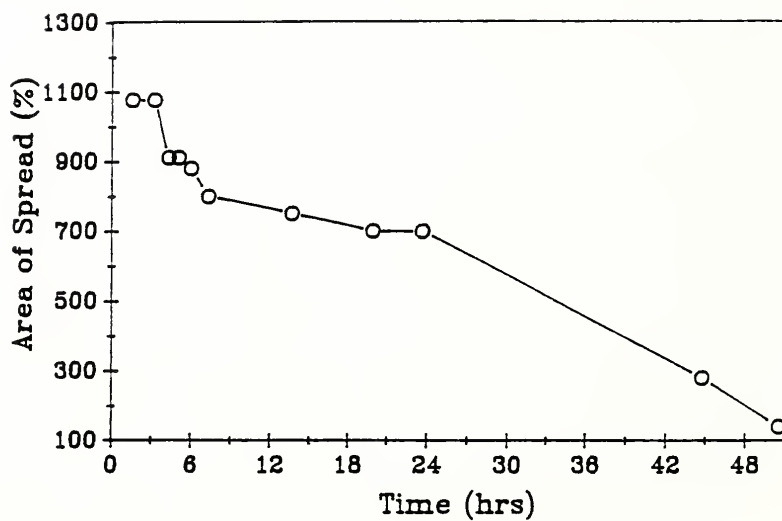


Fig. 5.5-1 Area of spread in mini-slump test vs. time for paste W with 2% melamine sulfonate superplasticizer M

— Removal of Superplasticizer from Solution

Fig. 5.5-2 shows the concentration of melamine sulfonate remaining in solution as a function of time over 2 days. The dosage of the superplasticizer M used here was 2%, equivalent to weight concentration of 40 g/L in the mix water. Three fourth of the admixture was initially removed from solution, and its concentration was reduced to about 10 g/L. However, this remaining concentration of the superplasticizer had been maintained up to 45 hours. The paste solution at 45 hours was still able to be recovered by the pressure filtering method.

As the experiment was carried out in the early stage of this research project, the interference on the melamine sulfonate determination by UV analysis due to the OH^- ions in the paste solution was not handled properly yet. The concentration of melamine sulfonate was determined without neutralizing the solution sample. Therefore the actual concentration of the polymer must be lower than the values indicated in the figure by approximately 15%. However, the time-dependent pattern of the absorption for this paste is considered to be figured out properly.

5.6 Findings

The findings from the experimental work on white cement W are summarized as follows.

1. The white cement used shows a peculiar chemical composition which is reflected in somewhat peculiar hydration characteristics. Cement W is described as a

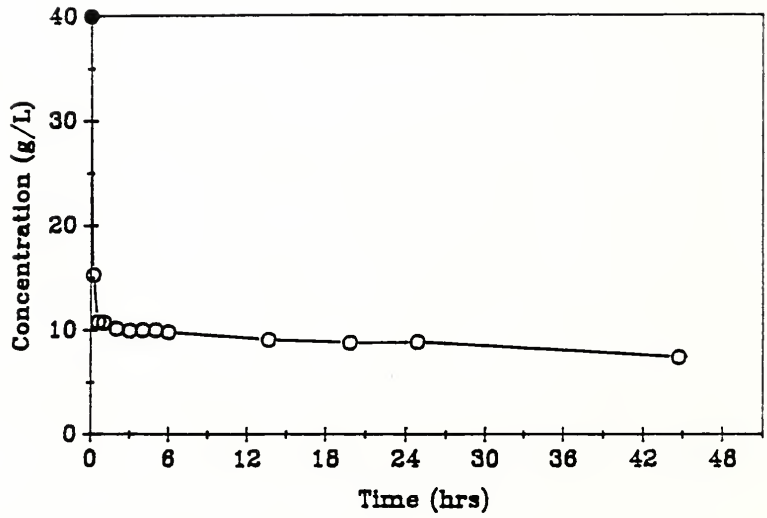


Fig. 5.5-2 Concentration of residual superplasticizer in mix water and pore solution vs. time for paste W with 2% melamine sulfonate superplasticizer M

cement of very low alkali content, low aluminate phase content, almost no iron content, and having insoluble anhydrite as the only form of calcium sulfate present. The solutions within the control paste WO have low ionic strength and low alkalinity.

2. Pastes of this white cement mixed only with a relatively pure naphthalene sulfonate superplasticizer exhibited rapid stiffening. This behavior is associated with the formation of a large amount of ettringite within about 15 minutes of the start of hydration, coupled with an almost complete removal of the superplasticizer from solution.
3. Two different naphthalene sulfonate superplasticizers produced significantly different early behaviors with the white cement. Pastes mixed with a less pure superplasticizer (superplasticizer A), that contains significant sodium sulfate impurity, did not stiffen but remained dispersed indefinitely. This behavior was reproduced using the pure superplasticizer (superplasticizer B) when an identical dosage of Na_2SO_4 impurity was added to it.
4. KOH added to the mix water affects the uptake of the naphthalene sulfonate from solution. With the less pure superplasticizer, the initial uptake increased as the amount of added KOH increased. The hydration reaction pattern of the pastes altered differently with different dosages of KOH, and the uptake of superplasticizer cannot be explained by one comprehensive mechanism.
5. Introduction of SO_4^{2-} ions into the mix water reduces the initial removal of

naphthalene sulfonate by the white cement. The presence of the sulfate ion in solution thus appears to lead to better performance by the superplasticizer.

6. Superplasticized pastes to which similar dosages of K_2SO_4 and Na_2SO_4 were added exhibited only slight differences in removal patterns of the naphthalene sulfonate from solution.
7. The cement paste mixed with naphthalene sulfonate and 0.6% KOH addition exhibited peculiar behavior. The polymer initially removed from solution by the solid phases was released back into solution, and then subsequently absorbed again.
8. As the dosage of KOH was increased, the rate of dissolution of insoluble anhydrite in the white cement was accelerated. With a high dosage (1.2%) of KOH, the superplasticized paste exhibited a different kind of quick solidification. From various items of evidence, such as the rapid formation of calcium hydroxide coupled with a complete lack of ettringite formation for the first two hours, the enhanced rate of insoluble anhydrite dissolution was attributed to the observed rapid precipitation of $Ca(OH)_2$ immediately after the start of the hydration. This precipitation was considered to be due to the high initial pH of the mix solution.
9. No hydrated form of calcium sulfate was found at any time in any of the hydrated pastes of the white cement. This was true regardless of the presence of superplasticizer or of added amounts of SO_4^{2-} or OH^- ions. For the pastes of moderately alkaline solution (i.e. with little or no added KOH), the slow rate of dissolution of anhydrite appears to restrict the sulfate ion concentration to values less than the

saturation level of calcium sulfate (80 meq/L). For the pastes of higher initial OH^- ion concentration, i.e. those with substantial amounts of added KOH, gypsum did not precipitate despite, the increased level of sulfate in solution.

10. A heavy dosage (2% by weight of cement) of a melamine sulfonate superplasticizer severely retarded the hydration of the white cement. The paste had been completely dispersed with bleeding for almost two days. The residual concentration of the admixture in paste solution remained reasonably high during the corresponding two day period.

CHAPTER SIX

EFFECTS OF SUPERPLASTICIZERS ON CEMENT "L" PASTES

In this chapter, broader effects of superplasticizers on cement pastes prepared with ASTM Type I cement L were investigated. This is a type I portland cement of moderate alkali content and typical chemical composition. Pastes examined included (a) the control mix (LO), (b) the mix LB, incorporating 1.55% naphthalene sulfonate superplasticizer B by weight of cement, and (c) the mix LM, incorporating 0.5% melamine sulfonate superplasticizer M. Analyses of both paste solution and solid specimens were carried out for specimens sampled periodically during the first day, and also at 1, 3, 7, and 14 days after mixing. All specimens were kept in sealed containers up to the time of sampling.

The lower concentration of melamine sulfonate used here was selected because of the very strong effect of this superplasticizer on the white cement described in the previous chapter. It was found that with a 2% dose setting of the white cement was delayed for two days and the amount remaining in solution at two days was still high. In consequence, in the work with cement L, the dosage of melamine sulfonate was reduced to 0.5%.

6.1 Result

6.1.1 Effects of Superplasticizers on Hydration

Fig. 6.1-1 illustrates the loss on ignition over the first day of hydration for the three mix series, LO, LB, and LX, and Fig. 6.1-2 shows the pattern of Fig. 6.1-1 extended to 14 days. The loss on ignition data have been corrected for the superplasticizer absorbed by the solids. Results of conduction calorimetry analysis for these three mixes up to two days are shown in Fig. 6.1-3.

The loss of ignition data and calorimetry measurement for mix LB indicate the existence of a severe retarding effect of this heavy dosage of the superplasticizer B. The melamine sulfonate superplasticizer M, used at a much lower dose level, caused only modest retardation. From the longer term loss on ignition data, it is found that the retardation effect by superplasticizer B, appears to be converted to a permanent reduction in loss on ignition. This permanent reduction in ignition loss may be a reflection of a change in the composition of the hydration product, rather than of a permanent reduction in the amount of cement that will hydrate. For mix LM, loss on ignition was about the same as the control case at one day and became higher thereafter.

In Fig. 6.1-4, the mini-slump value is plotted as a function of time for the three series of mixes. Both superplasticizers greatly increased the spread, to an early level of about 1100% as compared to a level of the order of 300% - 400% without super-

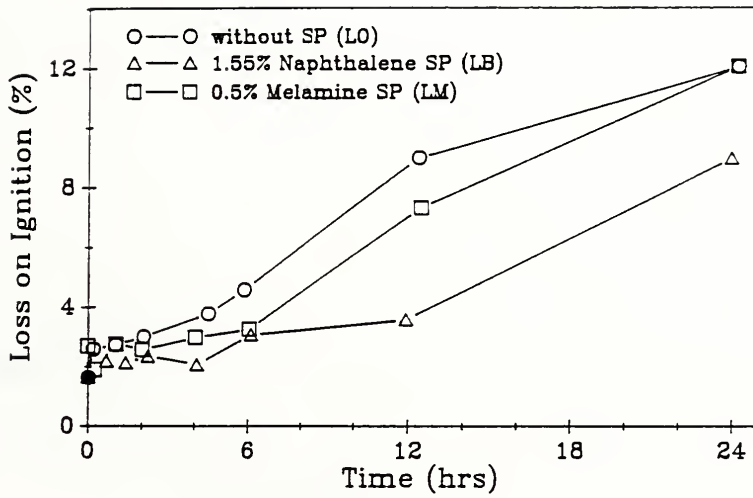


Fig. 6.1-1 Loss on ignition as a function of time up to 1 day for pastes of cement L without superplasticizer (LO), with 1.55% naphthalene sulfonate (LB), and with 0.5% melamine sulfonate (LM)

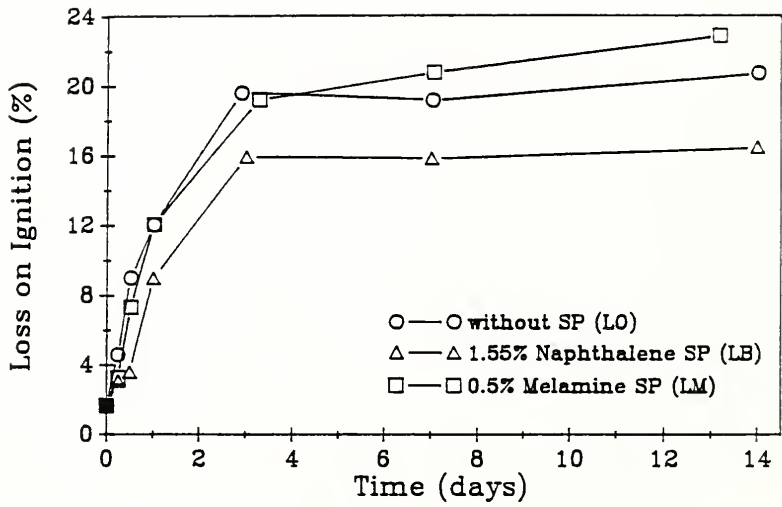


Fig. 6.1-2 Loss on ignition of pastes for periods extended to 14 days

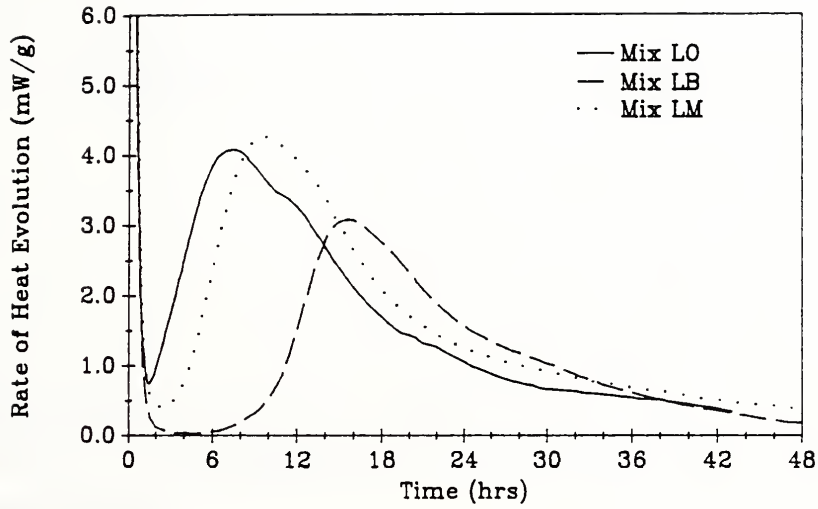


Fig. 6.1-3 Conduction calorimetric curves showing heat evolution vs. time for mixes LO, LB, and LM

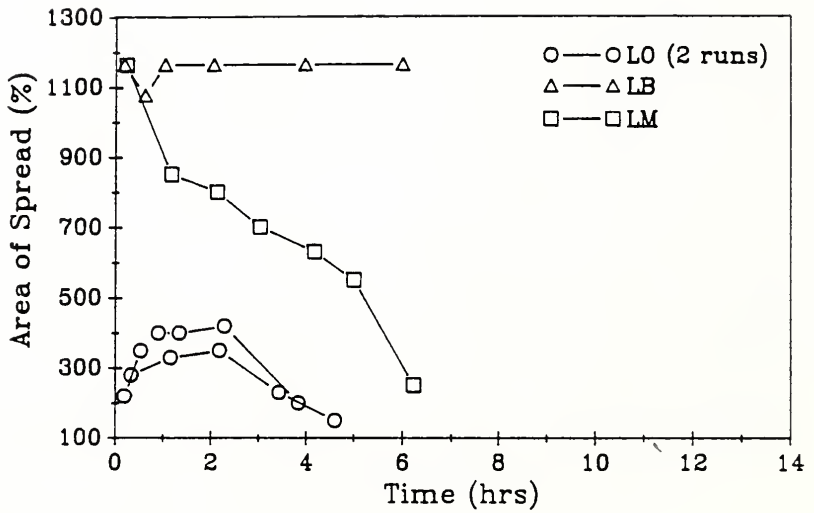


Fig. 6.1-4 Area of spread in mini-slump test vs. time for mixes LO, LB, and LM

plasticizer. The initial set time without superplasticizer was 5.5 hours, and after about 2 hours there was a progressive reduction in spread (fluidity). For the paste with a high dosage of naphthalene sulfonate the initial set time was delayed to 12.5 hours; the available data in Fig. 6.1-4 show that the high initial level of spread was maintained for at least 6 hours. In contrast, the lower dosage of melamine sulfonate produced only a modest retardation (initial set increases from 5.5 hours to 8.5 hours), and the spread percentage decreased rapidly from the starting level of over 1100% to only about 200% by 6 hours.

6.1.2 Control Paste Without Superplasticizer (LO): Solution and Solid Phase Analysis

6.1.2.1 Inorganic Ion Concentrations in the Paste Solution

Fig. 6.1-5 shows the concentrations of K^+ , Na^+ , Ca^{2+} , OH^- and SO_4^{2-} as functions of time over the first 24 hours of the control paste. The results of two replicate runs on different days are plotted, and are reasonably consistent. The pattern was that predicted for a low alkali cement paste from prior work, as presented recently by Diamond and Penko [77].

The concentrations of the alkali ions, Na^+ and K^+ , were stabilized quickly at levels of about 300 meq/L and 30 meq/L respectively. The concentration of Ca^{2+} rose immediately to about 40 meq/L, maintained almost constant for several hours, and then diminished to near zero between 12 and 24 hours.

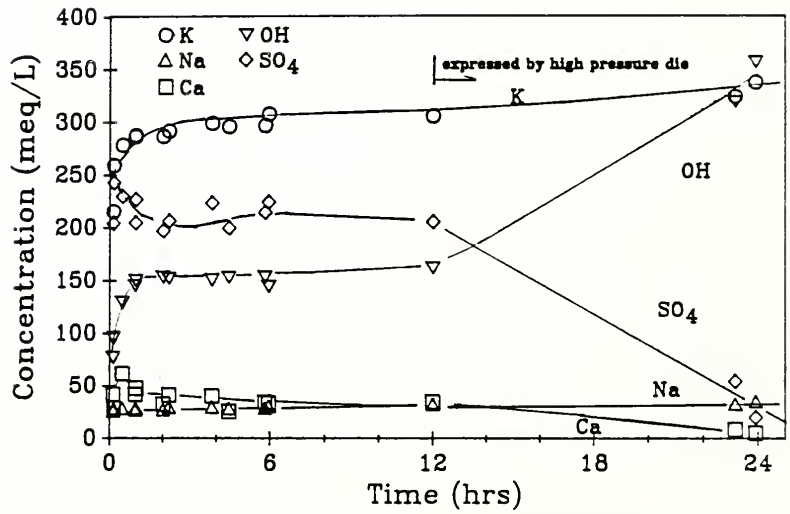


Fig. 6.1-5 Concentration of inorganic ions in mix water and pore solution vs. time in control paste (LO)

For the anions, the SO_4^{2-} concentration was maintained at a plateau of about 220 meq/L, then progressively decreased to about 20 meq/L after 12 hours. There was an increase in the OH^- ion concentration from 150 meq/L to 350 meq/L corresponding in both time and magnitude to this decrease of SO_4^{2-} .

Fig. 6.1-6 provides the same information as Fig. 6.1-5, but extended to 14 days. As expected, the Ca^{2+} and SO_4^{2-} ion concentrations were practically zero after the first day. The ions remaining in solution were K^+ , Na^+ , and OH^- ; for all of these, the concentration rose significantly between 1 and 3 days, and increased slightly thereafter. This uniform increase after 3 days is presumably due to reduction of solvent water caused by cement hydration.

Table 6.1-1 shows the sum of the cation concentrations and the sum of the anion concentrations for duplicate 1 day determinations and for three longer-time determinations for these LO control cement pastes. Each value of the algebraic difference between the sum of the anions and the sum of the cations seems to be within a range of reasonable experimental error. There are approximately equal numbers of net positive and net negative values, and the mean algebraic difference of the set is only +0.6 meq/L. This is only about 0.2% of the mean concentration of either cations or anions, strongly indicating that the analyses were correct and that no ion other than those reported was present in appreciable concentration.

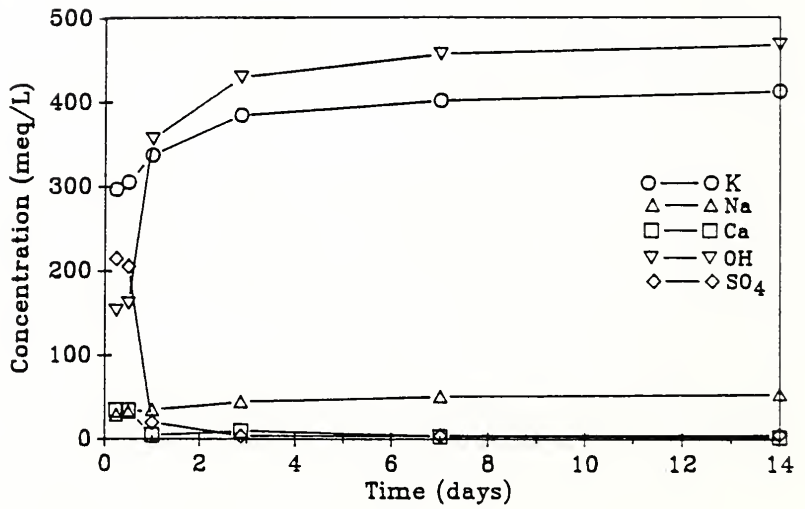


Fig. 6.1-6 Concentration of inorganic ions in pore solution vs. time for extended periods up to 14 days in control paste (LO)

Table 6.1-1 Experimental cation-anion balance in solutions for mix LO

Age	Σ Cations (meq/L)	Σ Anions (meq/L)	Difference (meq/L)
Run 1 (hr)			
0.15	282.7	280.8	+ 1.9
0.50	368.1	358.8	+ 9.3
1.00	363.6	376.7	- 13.1
2.23	361.9	357.9	+ 4.1
3.83	368.7	373.5	- 4.9
5.95	371.2	368.1	+ 3.1
23.17	364.9	372.9	- 8.0
Run 2 (hr)			
0.17	315.4	336.3	- 20.9
0.98	355.3	344.1	+ 11.2
2.02	345.8	347.9	- 2.0
4.47	349.4	346.6	+ 2.8
5.82	359.8	365.4	- 5.6
12.00	372.2	364.5	+ 7.7
23.92	377.6	375.0	+ 2.5
Run 2 (day)			
2.88	439.4	431.8	+ 7.6
7.00	455.9	457.6	- 1.7
14.00	469.2	473.8	- 4.5

6.1.2.2 Solid Phase Analyses

Fig. 6.1-7 exhibits the results of analyses for CaSO_4 bearing phases carried out in the corresponding solid samples over the first 24 hours. The initial form of calcium sulfate in cement L was found to be entirely calcium sulfate hemihydrate. The CaSO_4 -bearing solid phases detected throughout the experiment were all in the hydrous forms, specifically hemihydrate, gypsum, and ettringite. Those compounds were quantified by DSC analysis, and the quantity of each compound found was re-expressed in terms of the ratio of its SO_4 content to the ignited weight of the compound. In this way the amount of each compound can be visualized in terms of the fractional content of the total sulfate originally present in the cement. The results of two replicate runs on different days are presented on the figure. It is seen that ettringite determinations are highly reproducible as a function of time, and that the residual gypsum determination are reasonably so.

The calcium sulfate hemihydrate found in the original cement corresponded to 1.3% SO_4 content (compared to a total SO_4 analysis of 3.76% for the cement). This hemihydrate analysis was done several times on different days with the same result. No other form of calcium sulfate was detected either by x-ray diffraction or by DSC analysis. However, soluble anhydrite ($\gamma\text{-CaSO}_4$) may be present in an unknown amount; this phase contains only a trace of water and would escape detection by both DSC and x-ray diffraction, since its crystal structure is virtually identical to that of hemihydrate. Its quantitative assessment by x-ray diffraction in the presence of hemihydrate is extremely difficult and was not attempted. Additional sulfate may have

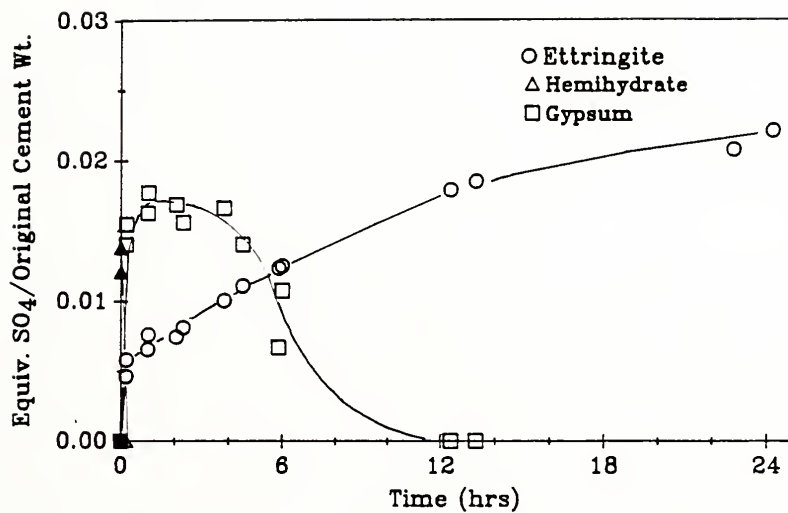


Fig. 6.1-7 Content of sulfate-bearing phases in paste solids vs. time up to 1 day for control paste LO
(Percentage of each solid phase re-expressed in terms of its SO_4 content.)

been present in the clinker as alkali sulfate, alkali calcium sulfate, and in solid solution in some of the cement components.

Within the first 10 minutes it was found that the hemihydrate had completely disappeared. Gypsum had formed equivalent to 1.5% SO_4 content (as compared with the 1.3% SO_4 equivalent content of hemihydrate). The gypsum content was maintained at the 1.5% SO_4 level until about 4 hours and then it progressively decreased. Gypsum was not detected in the solid at 12 hours but it might have been completely gone at any time after the previous determination at 6 hours.

An initial formation of ettringite in the first 15 minutes was detected, amounting to around 0.5% SO_4 . Then the ettringite content continued to increase rapidly to around 12 hours, and then more slowly to 24 hours.

The relationship of ettringite formation to the heat evolution curve (Fig. 6.1-3, mix LO) was not entirely clear. However, the onset of rapid ettringite formation at about 2 hours seems to coincide with the second peak of the heat evolution curve. This second major peak of hydration of the control mix LO had a small shoulder around 12 hours. Some researchers, such as Taylor [6], considered such a shoulder to be caused by the onset of secondary ettringite formation, rather than to conversion of ettringite to monosulfate. Since ettringite formation has been continuous and rapid since about 2 hours and the shoulder appears at 12 hours, the results rule out the former hypothesis in this case. The latter hypothesis is also obviously incorrect, since no monosulfate was detected.

Fig. 6.1-8 shows the same patterns extended to 14 days. The ettringite did not seem to increase during the longer term period and was constant at an equivalent SO_4 content of around 2.2%. No calcium aluminate monosulfate hydrate was found over the entire 14 days.

Table 6.1-2 illustrates the total balance of sulfate accounted for at each age. The initial hemihydrate content was determined by DSC using as a calibration mixtures of well crystallized hemihydrate with another cement having anhydrite. Any soluble anhydrite would not have been tallied. After hydration began, the sum of the SO_4 content in the solid phases accounted in the analysis (ettringite, gypsum, and hemihydrate) plus that in the solution phase increased from about 2.5% SO_4 to almost 3% SO_4 at about 5 hours. It then began to be progressively reduced, reaching about 2-1/4% at 1 day and then being maintained at about this level.

Some of the sulfate present is not accounted for due to the difficulty of quantitative analysis. Any alkali sulfate, alkali calcium sulfate, and soluble anhydrite present in the original cement are not accounted for in the calculation; thus the hemihydrate sulfate content of 1.38% at time zero obviously does not represent the total sulfate in the system. Alkali sulfates and alkali calcium sulfates dissolve very rapidly; thus the sulfate in the solution phase at early stages is mostly derived from these phases. It is also known that the sulfate ion is later incorporated to some extent by amorphous C-S-H gel as it develops. This is not easily quantified, and is believed to be responsible for the reduction of the sum of sulfate contents determined after the rapid cement hydration has begun.

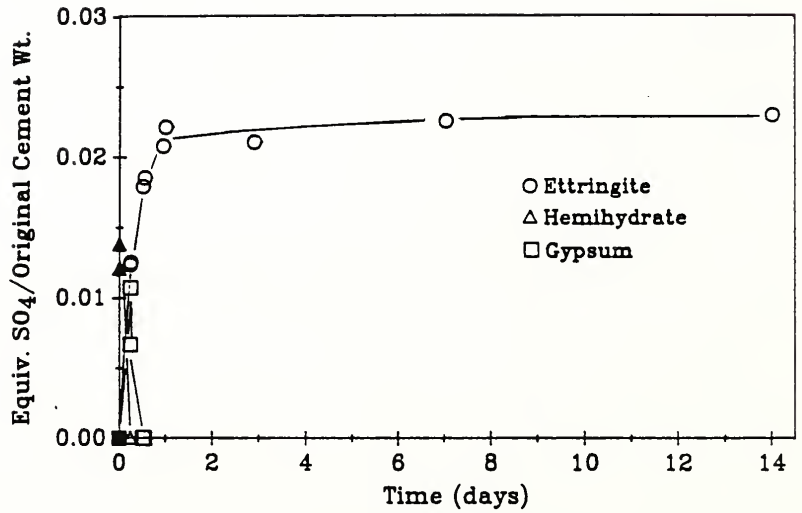


Fig. 6.1-8 Content of sulfate-bearing phases in paste solids vs. time for extended periods up to 14 days for control paste LO

Table 6.1-2 Total balance of sulfate-bearing phase for mix LO*

(Percentages expressed in terms of equivalent SO_4 content)

Age (hr)	Hemihydrate (%)	Gypsum (%)	Etringite (%)	Σ Solid (%)	Solution (%)	Total (%)
0.00	1.38	0.0	0.0	1.38	0.0	1.38
0.20	0.0	1.40	0.46	1.87	0.58	2.44
1.02	0.0	1.63	0.66	2.28	0.48	2.76
2.07	0.0	1.69	0.74	2.43	0.47	2.90
4.52	0.0	1.40	1.11	2.51	0.47	2.97
5.87	0.0	0.67	1.24	1.90	0.51	2.41
12.38	0.0	0.0	1.79	1.79	0.49	2.28
24.26	0.0	0.0	2.21	2.21	0.04	2.26
(day)						
2.90	0.0	0.0	2.10	2.10	0.01	2.11
7.02	0.0	0.0	2.25	2.25	0.00	2.25
14.02	0.0	0.0	2.29	2.29	0.01	2.31

* The total SO_4 content of the cement, separately determined, was 3.76% as SO_4 .

With regard to the SO_4^{2-} ion concentration in solution, this was found to be approximately constant at a plateau level (corresponding to about 0.5% SO_4) until 12 hours. The progressive drop of the sulfate ion from this plateau level occurred after the secondary gypsum was consumed totally. At the same time the hydroxide ion concentration started a corresponding increase to higher levels. The timing of this sudden drop of the sulfate concentration was not until much after the peak of heat evolution (7 hours), which implies that the phenomenon is not associated with hydration but is initiated by the depletion of solid gypsum. It is evident that additional crystalline ettringite is formed between 12 and 24 hours, even after the gypsum content has been exhausted (Fig. 6.1-7). The SO_4^{2-} ion for this additional ettringite came from the existing stock of dissolved SO_4^{2-} at 12 hours, as seen in Fig. 6.1-5.

6.1.3 Paste with Naphthalene Sulfonate Superplasticizer (LB): Solution and Solid Phase Analysis

6.1.3.1 Removal of Superplasticizer from Solution

Fig. 6.1-9 indicates the concentration of superplasticizer remaining in solution as a function of time up to one day, and the results of three replicate runs on three different days. About one quarter of the heavily dosed superplasticizer was removed from solution immediately; then the concentration was maintained at a constant level for about 6 hours. Most of the residual naphthalene sulfonate was then removed from solution between 6 and 14 hours, which corresponds to a major rise in the loss on ignition as

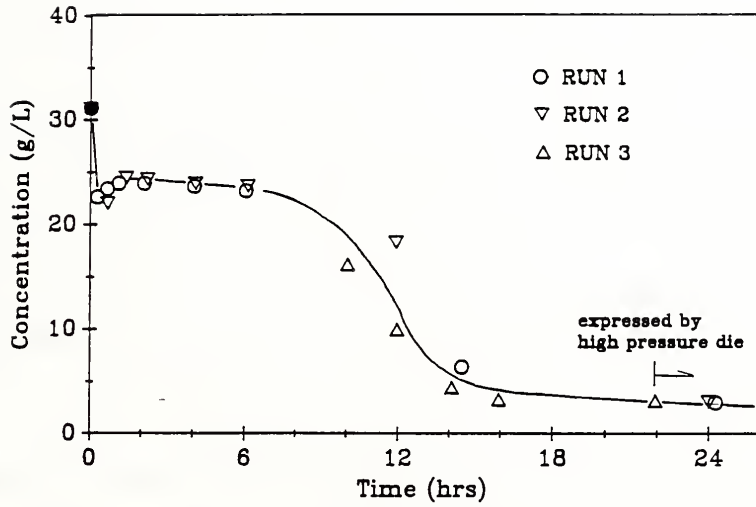


Fig. 6.1-9 Concentration of residual superplasticizer in mix water and pore solution for naphthalene sulfonate bearing pastes (LB) up to 1 day

indicated in Fig. 6.1-1, and to the major peak of the heat evolution curve in Fig. 6.1-3. The removal of the admixture from the liquid phase is attributed probably to either adsorption on or incorporation in the hydration products being produced. As illustrated in Fig. 6.1-10, only a low concentration of superplasticizer remained in solution by 1 day, and this low level persisted until 14 days.

6.1.3.2 Inorganic Ion Concentrations in the Paste Solution

Fig. 6.1-11 shows the changes in inorganic ion concentrations until 24 hours for the mix LB. Again the results of three replicate runs on different days are shown.

The original mix water with the dissolved superplasticizer contains considerable concentrations of inorganic ions (shown as filled symbols in Fig. 6.1-11). The ion with the highest concentration was 120 meq/L of Na^+ . There was a concentration of 20 meq/L of Ca^{2+} , about 5 meq/L of SO_4^{2-} , and a very little K^+ (2 meq/L). The OH^- ion is not found in measurable concentration. These ions are derived from the superplasticizer.

Paste solutions recovered at early ages with the admixture show a large difference in the Na^+ ion concentration. This is seen to be maintained at about 150 meq/L with superplasticizer present, much higher than previously found for the mix LO without superplasticizer, which was only about 40 meq/L. The additional sodium is derived from the admixture, as will be discussed later.

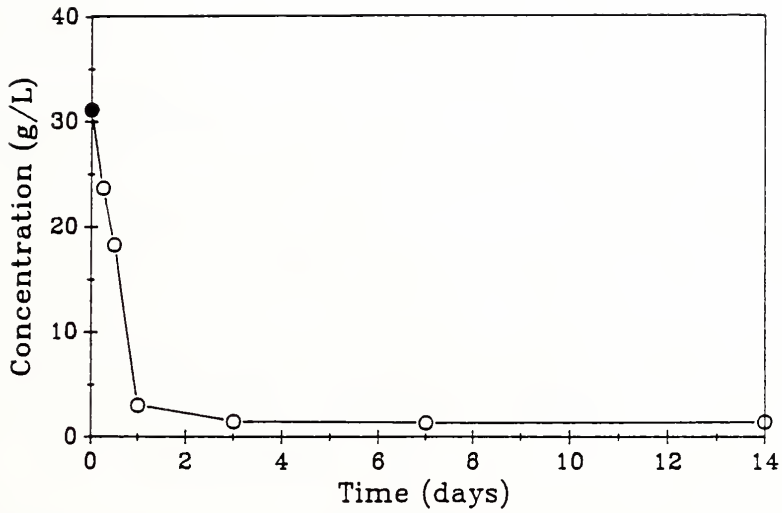


Fig. 6.1-10 Concentration of residual superplasticizer in pore solution of LB pastes for extended periods up to 14 days

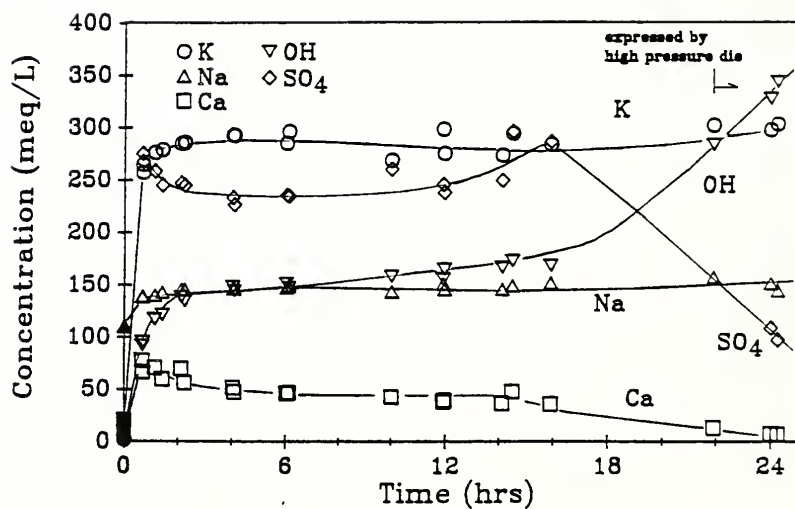


Fig. 6.1-11 Concentration of inorganic ions in mix water and pore solution vs. time in paste with naphthalene sulfonate superplasticizer (LB)

The K^+ ion concentration followed approximately the same pattern for the present data as was previously seen without superplasticizer, both being close to 300 meq/L at first, and trending slightly upward. The Ca^{2+} ion concentrations showed were slightly higher than those previously found, but showed a similar decreasing trend with time.

There was a significant difference in the two patterns for the SO_4^{2-} ion. The SO_4^{2-} ion was released to an initially higher concentration with the superplasticizer present (270 meq/L compared with about 230 meq/L). Then it was gradually reduced to the plateau over the first 12 hours but its plateau concentration level was higher with the admixture. There was even a small increase in SO_4^{2-} concentration at around 14 hours before the expected decline. The residual concentration at 24 hours for the paste with admixture was significantly higher than that in the control paste.

The OH^- ion concentration pattern with time was similar for both the superplasticized and control pastes.

Fig. 6.1-12 shows the longer term pattern for the superplasticizer-bearing paste. All the concentrations for the ions remaining in solution were approximately stabilized by 3 days and the increases in alkali ions and OH^- ion concentrations thereafter were much slower. The K^+ ion concentration level was about 50 meq/L higher for the control paste than for the superplasticized paste. For the Na^+ ion, the plateau concentration level was about 120 meq/L higher with the naphthalene sulfonate than without. The OH^- ion concentrations leveled off by 3 days to about a 50 meq/L higher level with the superplasticizer. Both SO_4^{2-} and Ca^{2+} ions were negligible after 3 days.

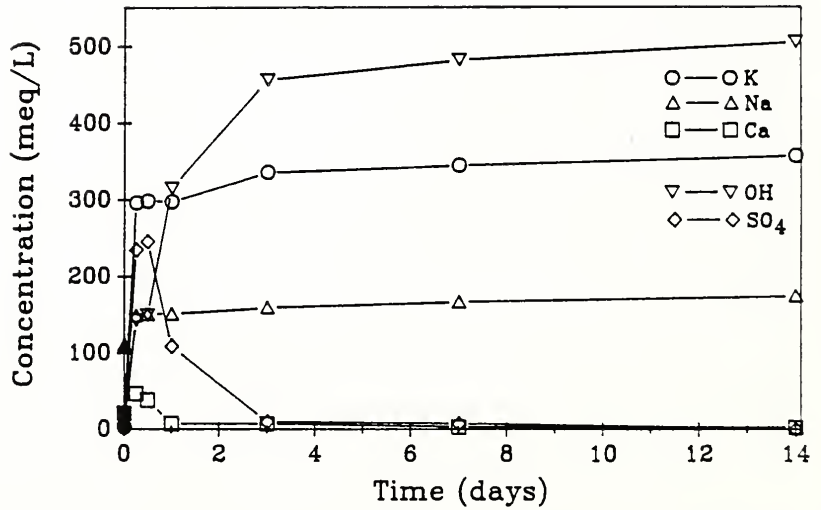


Fig. 6.1-12 Concentration of inorganic ions in pore solutions of naphthalene sulfonate bearing pastes (LB) vs. time for extended periods up to 14 days

Table 6.1-3 shows the sum of cations and anions for these pastes with superplasticizer. It is apparent that the balance previously found in the control pastes (Table 6.1-1) is not present here. Rather there were a large excess of cations present throughout the experiment, staying over 100 meq/L for the first 4 hours, and then dropping down progressively to around 20 meq/L at 24 hours. For pastes older sample than one day, only a small excess of cations was observed.

This lack of balance is apparently due to the residual concentration of the superplasticizer in the solution. While the separate inorganic ions have been accounted for, the negative $-\text{SO}_3^-$ (sulfonate) sites on the naphthalene sulfonate polymer chain remaining in solution have been neglected in the calculation. The naphthalene sulfonate superplasticizer B is a mostly sodium salt of what should be regarded as polymerized naphthalene sulfonic acid, i.e. a polymer bearing ionizable $-\text{SO}_3^- \text{Na}^+$ sites. This was confirmed by the previous analysis of the original mix water for the superplasticized paste. This Na^+ ion was released into the paste solution and was taken account into the sum of the cations, whereas the residual sulfonates associated with the dissolved polymer chains have not been considered yet. This "polymer anion" should be included to the charge balance.

Table 6.1-3 also shows the superplasticizer concentration in the solution phase. Assuming that all of the $-\text{SO}_3^-$ sites are fully neutralized by the cations determined, and that they are 100% ionized, the "polymer anion" concentration in the solution phase can be approximately equated to the excess cation concentration. If this is so, one should be able to estimate the charge "density" (meq/g) of the dissolved polymer

Table 6.1-3 Experimental cation-anion balance in solutions for mix LB

Age	Σ Cations (meq/L)	Σ Inorganic Anions (meq/L)	Difference (meq/L)	Polymer Conc. (g/L)	Calculated Charge Density* (meq/g)
Run 1 (hr)					
0.00	120.0	6.2	+ 113.7	31.5	3.61
0.67	480.4	368.4	+ 112.0	23.7	4.73
1.12	486.2	376.9	+ 109.3	24.2	4.51
2.10	500.1	387.1	+ 113.0	24.2	4.66
4.03	490.4	383.2	+ 107.2	24.0	4.48
6.03	477.8	388.3	+ 89.5	23.5	3.81
14.48	490.8	468.6	+ 22.2	6.5	3.44
24.25	453.8	441.0	+ 12.8	3.0	4.26
Run 2 (hr)					
0.00	133.6	4.9	+ 128.7	31.5	4.09
0.68	462.4	361.3	+ 101.1	22.3	4.54
1.40	481.2	361.8	+ 119.4	24.8	4.82
2.23	487.2	377.3	+ 109.9	24.6	4.46
4.08	486.0	365.6	+ 120.4	24.2	4.97
6.12	491.5	379.7	+ 111.7	24.0	4.66
11.92	486.6	399.2	+ 87.5	18.5	4.73
24.00	455.5	434.9	+ 20.6	3.0	6.77
Run 2 (day)					
3.01	502.1	483.6	+ 18.4	1.5	(12.28)
7.01	514.1	503.3	+ 10.8	1.4	(7.94)
14.00	533.7	529.2	+ 4.5	1.5	(3.11)

* of residual superplasticizers in solution.

by dividing the surplus cation concentration (meq/L) by the weight concentration of superplasticizer (g/L) at the same time. Such estimates are shown in the rightmost column of Table 6.1-3. These values are almost constant, at an average value of 4.8 meq/g over the first day.

Fig. 6.1-13 shows a combination plot of (a) remaining weight concentration of naphthalene sulfonate in the liquid phase vs. time and (b) the excess cation charge difference calculated vs. time. The left and right y-axis are excess cation concentration and superplasticizer weight concentration respectively. The two axes are aligned by the average charge density calculated for the "polymer anion" in solution over the first day, as 4.8 meq/g. The correlation of these two parameters is evidently high.

6.1.3.3 Solid Phase Analyses

Fig. 6.1-14 shows the data corresponding to Fig. 6.1-7 for the present superplasticized cement pastes. The results of two replicate runs and one partial run on different days are plotted.

The compounds detected were the same as for the control cement pastes. However the deviation of the data points in replicate runs seems to be larger, probably because the polymer adsorption affects the crystallization process and results in slightly different amounts of combined water of the hydration products.

In the presence of the superplasticizer, the rate of the conversion from hemihydrate to gypsum was slowed down. Hemihydrate was still observed in the 10 minute

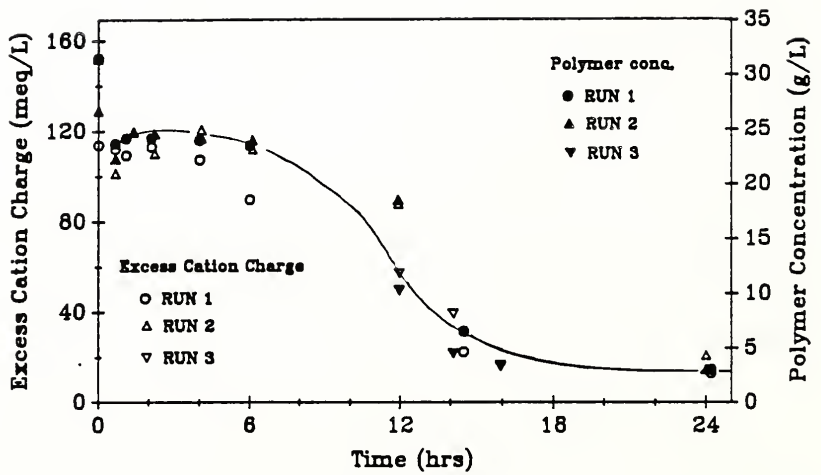


Fig. 6.1-13 Association of superplasticizer concentration and apparent excess cation charges in liquid phase for mix LB

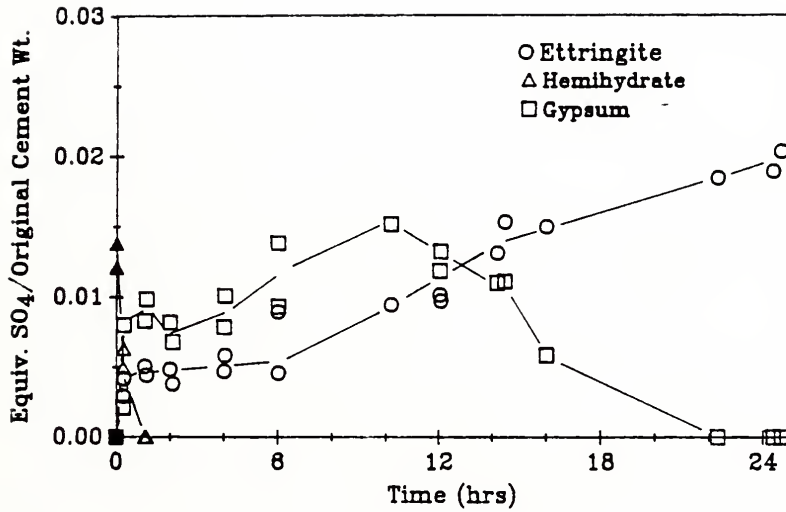


Fig. 6.1-14 Content of sulfate-bearing phases found in paste solids vs. time up to 1 day for naphthalene sulfonate bearing pastes (LB)
(Percentage of each solid phase re-expressed in terms of its SO₄ content.)

sample, but it was fully converted to gypsum by 1 hour. However, the actual amount of gypsum produced in this period was reduced with the superplasticizer. The amount of gypsum produced immediately after the mixing was not as high as in the control mix, being only around 0.8% (expressed in terms of the SO_4 content), while it was around 1.5% for paste without superplasticizer. It seems that the superplasticizer is absorbed by hemihydrate particles, as well as by the hydrating clinker phases and their products, and this may retard their dissolution and subsequent formation of gypsum.

The gypsum content gradually increased to a maximum of 1.5% SO_4 content at around 10 hours. Then it decreased gradually and reached zero sometime between 16 and 22 hours. This gypsum depletion preceded the start of the drop of the sulfate ion concentration in the solution phase, as was previously observed in the control case.

Ettringite was found in the 15 minute sample at about 0.5% as SO_4 , and its concentration was constant for next 4 hours. This is different from the time pattern of ettringite production when no superplasticizer was present (Fig. 6.1-7). In that case there was a continuous increase in ettringite content and no plateau. At approximately 4 hours with the superplasticizer, the ettringite content started to increase, and it increased almost linearly and reached about 1.95% SO_4 content at one day.

Fig. 6.1-15 shows the same patterns for times extended to 14 days. The CaSO_4 -bearing compound detected throughout this period continued to be entirely ettringite; no monosulfate was found. Though there was some variation, the trend was such that

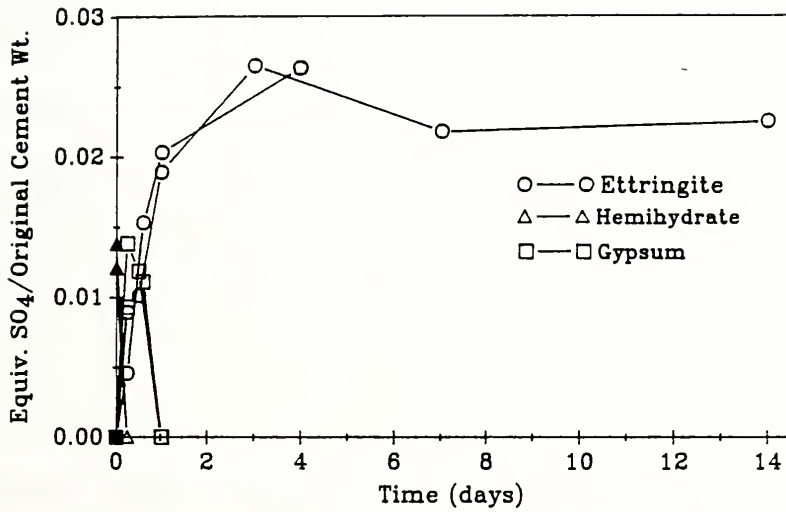


Fig. 6.1-15 Content of sulfate-bearing phases found in paste solids vs. time up to 14 day for naphthalene sulfonate bearing pastes (LB)

the ettringite amount reached a maximum of about 2.6% SO_4 content at 3 days. It then appeared to decrease to about 2.1% SO_4 content and remained constant from 7 days onward.

Table 6.1-4 shows the balance of the sulfate phases for the superplasticized paste. The combined SO_4 contents determined in recognized phases are somewhat lower than the corresponding totals for the paste without admixture. Between 1 hours and 4 hours, the total sulfate accounted for averaged 1.9% SO_4 as compared to almost 3% previously (Table 6.1-2). A much smaller amount of secondary gypsum is the main reason for the smaller total value here. It is presumed that some of the calcium sulfate at this stage existed in an amorphous phase, perhaps associated with absorbed layers of the polymer. Subsequently, the total SO_4 increased to around 2.8% at 6 and 12 hours reflecting in part a significant increase in the gypsum content. At later ages the total then decreased, presumably reflecting incorporation of some SO_4 with the C-S-H hydration products.

6.1.4 Paste with Melamine Sulfonate Superplasticizer (LM): Solution and Solid Phase Analysis

6.1.4.1 Removal of Superplasticizer from Solution

Fig. 6.1-16 illustrates the concentration of the melamine sulfonate superplasticizer M remaining in solution as a function of time for 24 hours. The dosage of the superplasticizer M used here was 0.5%, leading to an initial concentration of about 10 g/L.

Table 6.1-4 Total balance of sulfate-bearing phase for mix LB

(Percentages expressed in terms of equivalent SO_4 content)

Age (hr)	Hemihydrate (%)	Gypsum (%)	Ettringite (%)	Σ Solid (%)	Solution (%)	Total (%)
0.00	1.38	0.0	0.0	1.38	0.01	1.39
0.28	0.63	0.80	0.42	1.84	0.64	2.48
1.05	0.0	0.83	0.51	1.33	0.58	1.91
1.98	0.0	0.82	0.48	1.30	0.58	1.89
4.00	0.0	0.78	0.47	1.25	0.53	1.79
6.00	0.0	1.38	0.89	2.28	0.56	2.83
12.03	0.0	1.18	1.01	2.20	0.58	2.78
24.38	0.0	0.0	1.89	1.89	0.26	2.15
(day)						
3.03	0.0	0.0	2.64	2.64	0.02	2.67
7.03	0.0	0.0	2.18	2.18	0.01	2.19
14.02	0.0	0.0	2.25	2.25	0.01	2.27

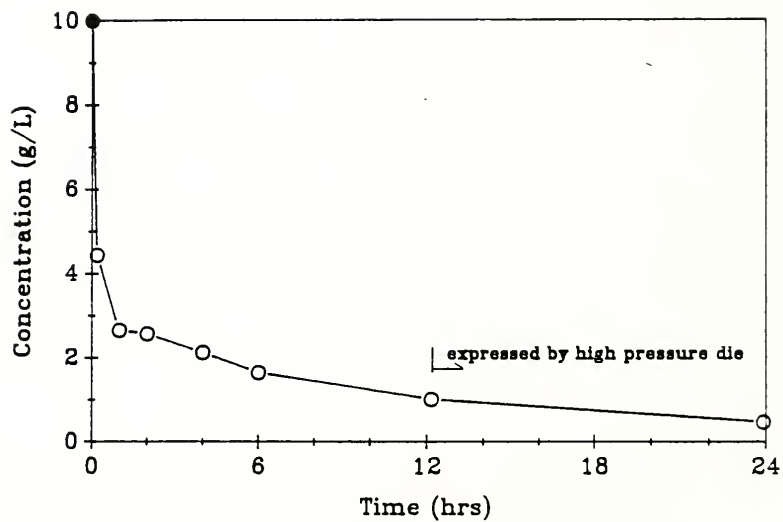


Fig. 6.1-16 Concentration of residual superplasticizer in mix water and pore solution for melamine sulfonate bearing pastes (LM) up to 1 day

Due to this light dosage, the proportion of the admixture initially removed by the cement was higher than for the mix LB. However, the pattern of the absorption with time is the same as was found with naphthalene sulfonate: a sequence of immediate absorption, plateau, second-stage absorption, and retention of a residual low concentration were observed in the pattern. For pastes older than 1 day, the residual concentration of the superplasticizer was only about 0.4 g/L, as shown in Fig. 6.1-17.

6.1.4.2 Inorganic Ion Concentrations in the Paste Solution

Fig. 6.1-18 shows the time dependent concentration of the inorganic ions up to 1 day. The general pattern is similar to the control mix case shown in Fig. 6.1-5, presumably because the light dosage did not appreciably interfere with early cement hydration, or delay its heat evolution peak very much.

However, similar to the effect found for the naphthalene sulfonate superplasticizer in the LB series, it was found here that the initial concentration level of the Na^+ ion was higher than without admixture, this time about 40 meq/L higher. This Na^+ concentration remained almost constant for the first 24 hours. This lesser enhancement in Na^+ concentration here as compared with LB pastes was proportional to the lesser dosage of the superplasticizer used.

It was found that the sulfate ion concentration here was a little higher at the plateau than was that for the control paste. The residual concentration of sulfate at 24 hours was also a little higher than that in the control case. The other inorganic ions,

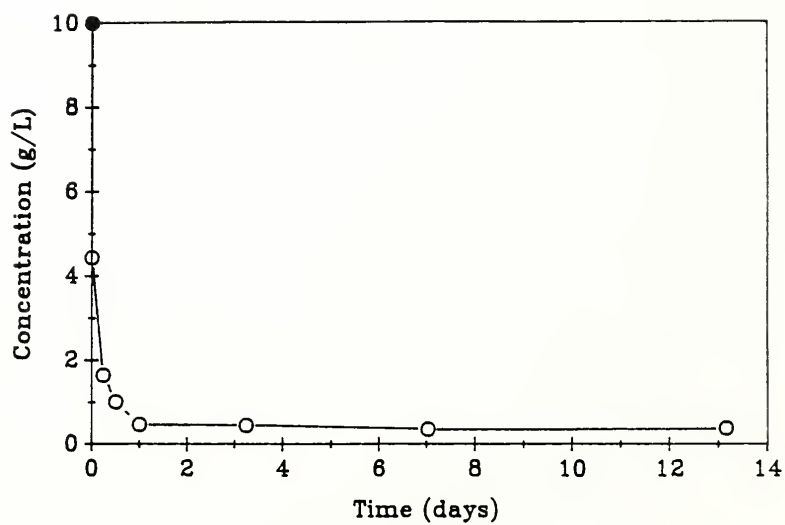


Fig. 6.1-17 Concentration of residual superplasticizer in pore solution of LM pastes for extended periods up to 14 days

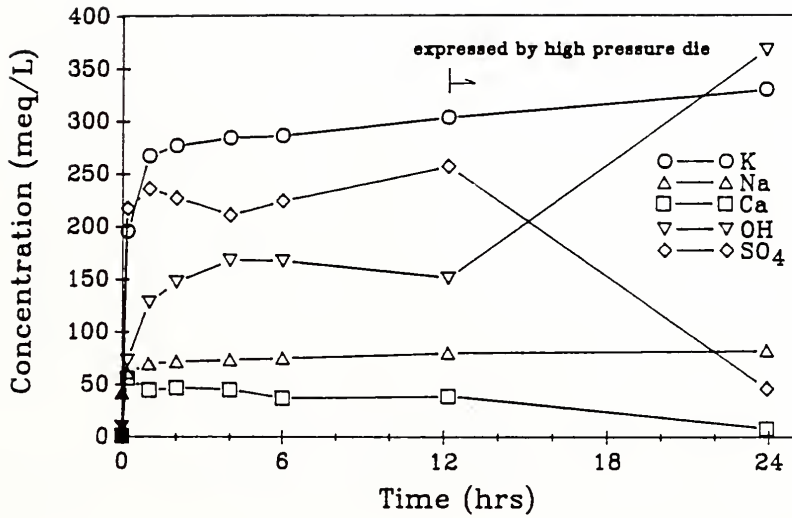


Fig. 6.1-18 Concentration of inorganic ions in mix water and pore solution vs. time in paste with melamine sulfonate superplasticizer (LM)

K^+ , Ca^{2+} , and OH^- , exhibited almost the same concentration-time patterns as those for the control mix without superplasticizer.

Fig. 6.1-19 shows the longer term pattern for the mix LM, for period up to 14 days. Differences from the control mix LO were shown, in that both Na^+ and OH^- ion concentrations are about 50 meq/L higher than those in the control mix without superplasticizer. This implies that the additional sodium introduced by the superplasticizer was converted into NaOH in the pore solution and remained as such. In contrast, the K^+ ion concentration was about the same as that for the paste without superplasticizer.

The same analysis of cation-anion-polymer balance was applied for the melamine sulfonate superplasticizer paste as previously applied for naphthalene sulfonate paste. Table 6.1-5 shows the same calculations as Table 6.1-1 for the mix LM. The trends of the residual excess cation and of the residual melamine sulfonate superplasticizer are similar for the first 24 hours of hydration, but there is much more scatter than was found previously for naphthalene sulfonate. The "charge density" calculated for the melamine sulfonate increased significantly over the first half day or so. However, subsequent calculations are essentially meaningless probably because of the low concentration of the residual melamine sulfonate.

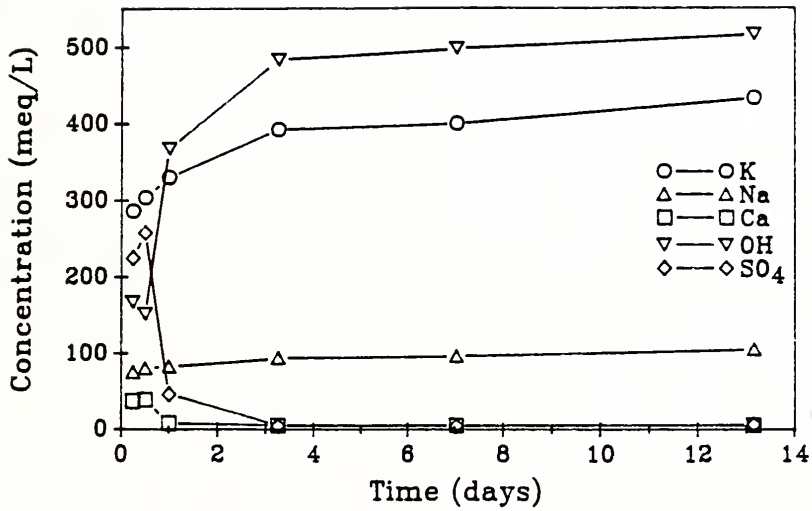


Fig. 6.1-19 Concentration of inorganic ions in pore solutions of melamine sulfonate bearing pastes (LM) vs. time for extended periods up to 14 days

Table 6.1-5 Experimental cation-anion balance in solutions for mix LM

Age (hr)	Σ Cations (meq/L)	Σ Inorganic Anions (meq/L)	Difference (meq/L)	Polymer Conc. (g/L)	Calculated Charge Density* (meq/g)
0.00	43.3	15.2	+ 28.1	10.0	2.81
0.20	312.3	297.5	+ 14.8	4.4	3.35
1.00	381.4	370.8	+ 10.6	2.6	3.99
2.00	395.7	381.6	+ 14.1	2.6	5.48
4.00	402.8	386.3	+ 16.5	2.1	7.80
6.00	397.9	398.4	- 0.4	1.6	- 0.27
12.17	422.5	414.5	+ 8.1	1.0	8.05
23.92	420.1	417.9	+ 2.2	0.5	4.75
(day)					
3.25	491.3	494.3	- 3.0	0.4	(- 6.66)
7.03	502.1	503.2	- 1.1	0.4	(- 3.14)
13.16	544.1	523.7	20.4	0.4	(55.19)

* of residual superplasticizers in solution.

6.1.4.3 Solid Phase Analyses

Fig. 6.1-20 shows the patterns of CaSO_4 -bearing phase for the mix LM until one day. Even with this lighter dosage of melamine sulfonate superplasticizer, the initial dissolution of hemihydrate was slowed, and residual hemihydrate was detected even at 15 minutes. The production of gypsum was also slowed somewhat. However, similar to the control paste, the gypsum was gone sometime between 6 and 12 hours. The reduced superplasticizer dosage as compared to the mix LB obviously resulted in much less retardation; in consequence, the gypsum disappeared far more quickly than in the LB pastes. Again a decline of the sulfate ion concentration was initiated after the total consumption of gypsum phase, i.e. starting after 12 hours.

The content of ettringite was increasing non-linearly in this period. Its formation rate was slower than that for the control mix LO for the first 6 hours. Then the rate of formation of ettringite increased rapidly, resulting in almost the same content as that for the control mix between 6 and 12 hours, and an excess over the control case at 24 hours.

Fig. 6.1-21 shows the time patterns up to 14 days for sulfate-bearing solids. Ettringite was the only calcium sulfate solid detected after 1 day. The ettringite concentration appeared to be almost constant at around 2.7% SO_4 after 2 days. It was found that the shape of the peak of ettringite in DSC for this mix LM made it harder to differentiate ettringite from C-S-H gel than was the case with mix LB. Experimental errors in this determination will be discussed later.

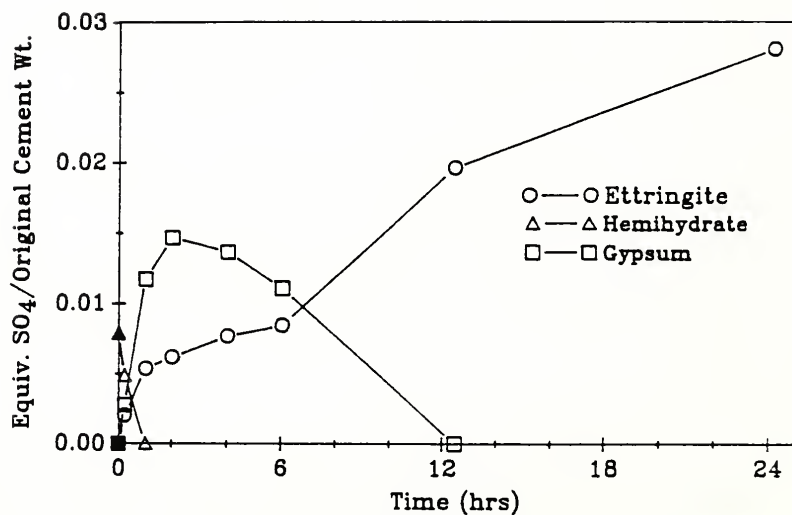


Fig. 6.1-20 Content of sulfate-bearing phases found in paste solids vs. time up to 1 day for melamine sulfonate bearing pastes (LM)
(Percentage of each solid phase re-expressed in terms of its SO₄ content.)

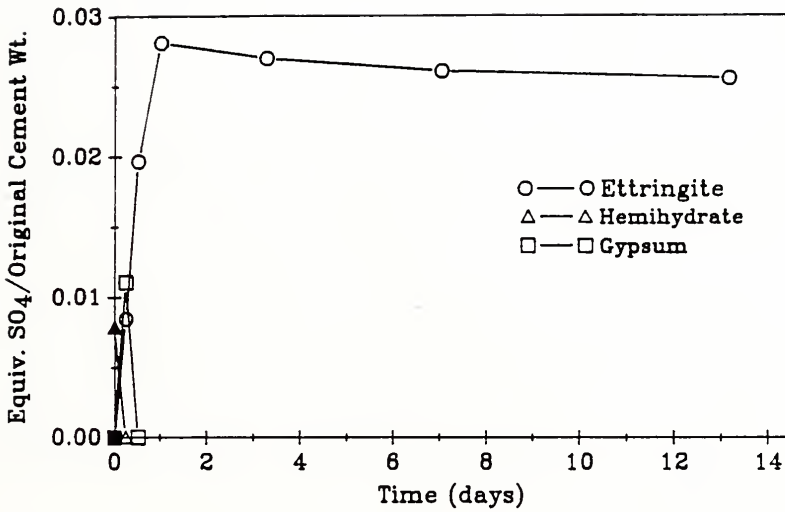


Fig. 6.1-21 Content of sulfate-bearing phases found in paste solids vs. time up to 14 day for melamine sulfonate bearing pastes (LM)

Table 6.1-6 shows the balance of the detected sulfate phases for the mix LM. The total sulfate accounted for rose during the first 2 hours to about 2.7% as SO_4 , and then fluctuated around this value. This total of detected SO_4 -containing phases was rather high, especially in later ages, due to the high content of ettringite detected.

6.2 Discussion

6.2.1 Nature of Residual Naphthalene Sulfonate Remaining in Solution

As pointed out in Chapter 3 and Chapter 4, the molecular weight composition of the naphthalene sulfonate superplasticizer can be estimated by the difference in UV light absorbance at two characteristic wavelengths. The actual naphthalene sulfonate concentration was determined throughout this study by using the extinction coefficient at the longer characteristic wavelength around 290 nm, designated ϵ_1 , because the absorbance at this wavelength is little affected by the degree of polymerization. The extinction coefficient at the shorter characteristic wavelength (218 nm), designated ϵ_s , alters with the composition of the monomer, and can also be estimated by the Beer-Lambert law,

$$\epsilon_s = \frac{A_s}{c \cdot l}$$

where A_s is the observed absorbance at the shorter wavelength, c is the concentration of the naphthalene sulfonate estimated by the absorbance at the longer characteristic wavelength, and l is the length of the light path. Here, the ϵ_s can be obtained for the

Table 6.1-6 Total balance of sulfate-bearing phase for mix LM

(Percentages expressed in terms of equivalent SO_4 content)

Age (hr)	Hemihydrate (%)	Gypsum (%)	Ettringite (%)	Σ Solid (%)	Solution (%)	Total (%)
0.00	1.38	0.0	0.0	1.38	0.01	1.39
0.23	0.48	0.28	0.21	0.97	0.54	1.51
1.03	0.0	1.17	0.54	1.71	0.58	2.29
2.02	0.0	1.47	0.62	2.09	0.56	2.65
4.03	0.0	1.36	0.77	2.13	0.52	2.66
6.05	0.0	1.11	0.85	1.96	0.56	2.51
12.47	0.0	0.0	1.97	1.97	0.63	2.60
24.25	0.0	0.0	2.81	2.81	0.12	2.93
(day)						
3.28	0.0	0.0	2.70	2.70	0.03	2.72
7.05	0.0	0.0	2.61	2.61	0.01	2.62
13.18	0.0	0.0	2.55	2.55	0.02	2.57

naphthalene sulfonate remaining in solution at any given time, and then the ratio of the ϵ_s to ϵ_l can be calculated. Fig. 6.2-1 illustrates this ratio ϵ_s/ϵ_l as a function of time for the mix LB.

Burk et al. [66] stated that the ratio of two extinction coefficients is linearly correlated to the percentage of monomer species in the naphthalene sulfonate superplasticizer. By using the equation of Burk et al., the data in Fig. 6.2-1 was also expressed in terms of the calculated percentage of monomer in the naphthalene sulfonate remaining in solution. The scale for this percentage is indicated on the right y-axis of the figure. The results indicated that the initial low percentage of monomer (about 12%) rose only a little after the first contact to around 19% at 12 hours. Then it jumped up to a much higher level of nearly 50% between 12 and 16 hours, and was constant after that.

The indication is that the large proportion of polymeric species initially present in the superplasticizer remained in the solution phase for several hours prior to set, and served to maintain the fluidity of the paste by its dispersing action. At the surge of the hydration around 12 hours, the polymeric species were preferentially adsorbed onto the newly formed hydration products, mostly C-S-H gel, whereas monomer was not absorbed and stayed in the liquid phase.

At later ages, the ratio ϵ_s/ϵ_l was found to be high, that is, the proportion of monomer in the solution phase was very high. Furthermore, low molecular weight polymeric species such as dimer, trimer, etc., which may compose about the same weight

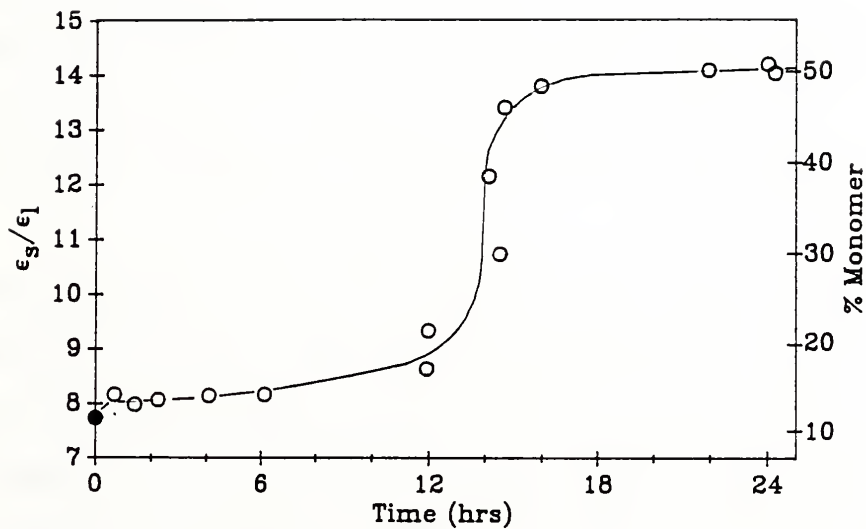


Fig. 6.2-1 Extinction coefficient ratio (ϵ_s/ϵ_l) and estimated corresponding percentage of monomers in residual naphthalene sulfonate found in paste solutions vs. time for LB pastes

fraction as monomer in the original superplasticizer, are also not taken up by the solid phases according to Burk et al. [66]. Assuming that 50 % of monomer plus about the same portion of dimer plus trimer are left in the solution phases older than one day, it appears that virtually no higher polymeric species exist in the older samples.

An attempt to convert the "polymer anion" concentration of naphthalene sulfonate to the equivalent inorganic anion at each age was shown at Table 6.1-3. It is noticed that the calculated charge density at time zero, i.e. that in the initial mixing water, is only about 3.6 meq/g. This is lower than the corresponding calculation for the early paste solutions, which seems to be fairly constant at approximately 4.7. The charge density measurement reflects the estimated number of sulfonate groups present per gram of polymer. This may vary considerably with chain length, and is only an average characteristic.

The apparent charge density became high irregular for the naphthalene sulfonate remaining in solution in paste samples older than 1 day. This is probably because the denominator of the calculation, the naphthalene sulfonate concentration, becomes so low that experimental error becomes unacceptably high. A direct measurement for dissolved sulfonate groups would obviously be a more appropriate alternative.

For the paste LM, a correlation between the polymer concentration and the excess positive charge were observed, but it was not as consistent, as seen by the variation in the apparent charge density of the melamine sulfonate in solution.

6.2.2 Effects of Superplasticizers on Inorganic Ion Concentrations in Solution

Significant effects of the superplasticizer were found for the early concentrations of SO_4^{2-} ions, OH^- ions, and Na^+ ions.

The increased level of SO_4^{2-} concentration maintained for a while in the pore solution with both superplasticizers as compared to the control paste may have some significance in terms of early reaction. The increased SO_4^{2-} level with superplasticizer can be attributed to smaller amounts of both gypsum first and then of ettringite formed in the dormant period, presumably due to absorption of the polymeric species on these crystals as they grow. This is clearly a transient effect; after a few days gypsum has been fully depleted and the sulfate concentration of superplasticizer-bearing and superplasticizer-free pastes are identically negligible.

It is confirmed from the analysis of pore solution after one day that the OH^- ion concentrations were higher in the pore solutions containing superplasticizers than in the pore solution without admixture. The actual OH^- ion concentration determined at 14 days were 460 meq/L without admixture, 520 meq/L with the naphthalene sulfonate, and the same 520 meq/L with the melamine sulfonate. This enhancement in alkalinity obviously due to the extra Na^+ ion derived from the superplasticizers. As was shown previously in Fig. 6.1-11, the concentrations of inorganic ions present in the original mix water for the superplasticized paste LB are 120 meq/L of Na^+ , 20 meq/L of Ca^{2+} , 5 meq/L of SO_4^{2-} , and a trace amount of K^+ . This extra Na^+ is brought into solution with the superplasticizer as the main cation, balancing the nega-

tively charged sulfonate group of the superplasticizer. As hydration proceeds, the polymer anions are absorbed to the solid phases, but the corresponding Na^+ ions remain in solution. A corresponding amount of OH^- ion is dissociated by hydrolysis action to neutralize the positive Na^+ ion charge. Presumably the same mechanism occurs in the melamine sulfonate pastes. When considering the use of alkali-bearing superplasticizer, higher pore solution alkalinity is thus to be expected. This may increase the susceptibility of the concrete to alkali-aggregate reaction.

6.2.3 Solid Phases

In all three cases, the commencement of the progressive decline of the sulfate ion concentration occurred independently to the general hydration process, but always followed the exhaustion of the secondary gypsum. This confirms the findings by Diamond [77] that this decay is triggered by approaching exhaustion of the residual gypsum. Retardation by superplasticizer absorption on the cement naturally postpones this condition.

The ettringite content in the two superplasticized pastes were smaller than that of the control paste up to 12 hours. As mentioned previously, it is considered that the superplasticizer interferes somewhat with the growth of the ettringite crystals that have incorporated some of the superplasticizer.

For all three pastes of cement L, the amount of ettringite leveled off after 3 days. This level of the ettringite concentration in mature pastes for mix LB was approxi-

mately 2.1% SO_4 equivalent, almost equal to the ettringite content of the corresponding control pastes. Thus the effect of the naphthalene sulfonate superplasticizer on the longer term ettringite content appears to be insignificant. For the paste LM, the long-term ettringite content (after 1 day) was 2.7% SO_4 equivalent, even higher than that for the control paste.

One of the most unexpected findings was that calcium aluminate monosulfate hydrate was not detected in any of the solid phases from mix L, even up to 14 days. The absence of monosulfate was confirmed both by checking the x-ray diffraction peak at d-spacing of $9.0\text{\AA}$, and by DSC analysis as follows.

To begin with, monosulfate was synthesized by following the method described by Suzuki et al. [78]. In that method, previously synthesized ettringite is boiled for 4 hours in the form of a dilute suspension of water:solids ratio 200. Though it was found that the product contained a little ettringite impurity, the DSC curve generated for specimens in the special DSC environment described earlier in this study, showed endothermic peaks at 82° , 145° , and 220°C which correspond to the dehydration peaks of monosulfate at 120° , 180° , and 290°C according to Suzuki et al.. The complete absence of monosulfate in all of these pastes was indicated by the fact that no endothermic peak was detected in the temperature range between 200°C and 300°C from any of the solid samples.

The normal partial conversion from ettringite to monosulfate at ages later than 1 day in cement pastes has been observed previously by many workers, for example by

Seligman et al. [79]. However, it was not observed here, even after the sulfate ion concentration in the pore solution had dropped to virtually zero later than 3 days. Some slight decreases in the ettringite contents were observed particularly in some superplasticized pastes, but those were not considered significant. Rather, the ettringite contents were nearly constant after 3 days for all three pastes of cement L.

This stability of ettringite appears to be attributable to the compositional characteristics of cement L. The cement L has only 5.38% of Al_2O_3 and 3.03% of SO_3 in the mill analysis; the proportion of SO_3 to Al_2O_3 is 0.56 by weight. This number suggests that the sulfate content compared to the aluminate content, is relatively high. This may promote the stability of the ettringite.

As is mentioned in the section 4.4.2, there is a complication in the quantitative determination of the ettringite in one day old and older samples for the cement L. As the paste hydrates, the overall DSC pattern shows a broad endothermic depression due to dehydration of C-S-H gel, so that the differentiation of ettringite from C-S-H gel becomes subject to some experimental uncertainty.

The basic rules for the differentiation were stated previously. However, the gradient of the DSC curve does not change abruptly in these older pastes. Thus the determinations of the starting point and end point become less distinctive than that for the younger pastes. Of the three pastes of cement L, the paste with melamine sulfonate exhibited the least sharp peak for ettringite, which was reflected in the larger variations of calculated ettringite contents for mix LM. Fig. 6.2-2 shows transition of the

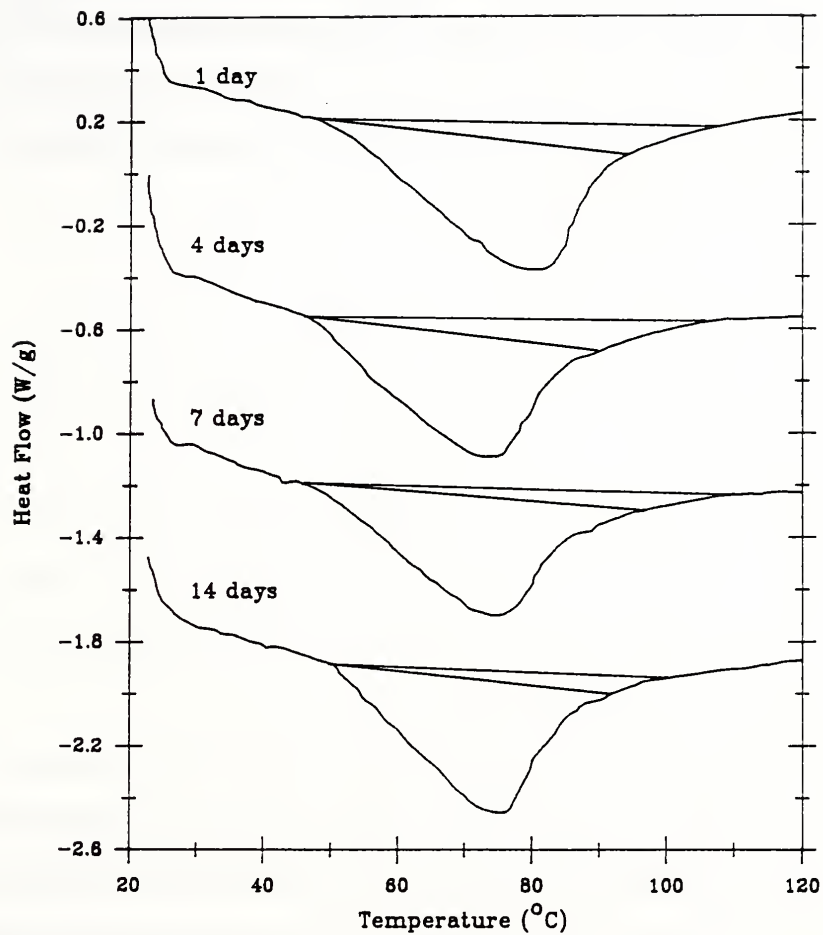


Fig. 6.2-2 DSC curves of the paste LM samples at 1 day to 14 days

DSC curves of older samples for the mix LM. For practical purpose with the ambiguous later specimens, a representative value was obtained by selecting the peak area of ettringite so chosen that the separation line drawn approximately in the middle of the maximum and the minimum cases shown in Fig. 6.2-2. The percentage difference between these extreme cases for samples older than one day averaged 2.7% for mix LO, 4.0% for mix LB, and 7.8% for mix LM.

6.3 Findings

The findings resulting from the experimental work carried out with cement L are as follows.

1. Both naphthalene sulfonate and melamine sulfonate had a retarding effect on the hydration of cement L. The effect was observed in calorimetry, in loss on ignition, in time of setting, in mini-slump, in the solution phase chemistry, and in the solid phase compound formation.
2. A method of incorporating organic ions into the charge balance calculation between positive and negative species in solution was developed and applied to both naphthalene sulfonate and melamine sulfonate bearing pastes. The apparent "charge density" of the naphthalene sulfonate polymer remaining in the paste solutions was fairly consistently estimated; that of the melamine sulfonate polymer was more variable.
3. The proportion of monomeric naphthalene sulfonate superplasticizer remaining in

paste solution was estimated by analyzing two characteristic peaks in UV absorption spectrum as a function of time. It was confirmed that the polymeric species in the superplasticizer were mostly adsorbed by the period of second hydration peak.

4. The sulfate ion concentration in paste solution at its "plateau" level (before the sudden drop) was higher in the presence of superplasticizers. This was a transient effect, attributed to retardation.
5. Significant increases were found in the Na^+ ion concentrations of pore solution with superplasticizers. These increases were due to Na^+ ions initially neutralizing sulfonate groups on the polymer.
6. It was found that the OH^- ion concentrations increased at later ages for pore solutions with superplasticizers to balance the excess Na^+ ions derived from the polymers.
7. It was found that the initial form of calcium sulfate in cement L was entirely hemihydrate. This was converted to gypsum almost immediately after the first contact with water. Gypsum stayed in the paste for about half a day. After that only detectable CaSO_4 -bearing compound was the ettringite. This conversion pattern was basically the same for this cement system with or without superplasticizers.
8. It was found useful to express the total of the solid CaSO_4 phases detected and the sulfate ions in solution in terms of sulfate content, as a function of time. The total sulfate quantified in this method was less than the total cement sulfate analysis because alkali or other clinker borne sulfates were not accounted for in the early

stages, and sulfate incorporated in C-S-H gel was not accounted for in the late stages. Nevertheless, changes in the total CaSO_4 phase detected were of interest in following the progress of the reactions.

9. The progressive decay of the sulfate concentration in solution from the "plateau level" in the liquid phase was preceded by the complete depletion of solid gypsum. This was common with or without the admixture.
10. No calcium aluminate monosulfate hydrate was detected in any of the cement L paste samples up to 14 days of age, even though the sulfate concentration in the pore solution was virtually zero after one day.
11. Ettringite determination by DSC analysis in the more mature samples was subject to a complication because of increasing amounts of C-S-H gel. This difficulty was enhanced in the system with superplasticizers and resulted in experimental errors, since the characteristic dehydration peak of ettringite lost its sharpness.

CHAPTER SEVEN

EFFECTS OF SUPERPLASTICIZERS ON CEMENT "S" PASTES

In this chapter, results are reported for studies similar to those previously described for cement L, but here carried out on another ASTM Type I cement, cement S. Cement S is a somewhat higher alkali cement than the previously studied cement L (0.85% Na_2O equivalent as compared to 0.56% Na_2O equivalent), and has a high content of MgO . The calcium sulfate here is in the form of a mixture of gypsum and hemihydrate.

The mixes described here include the control mix SO without admixture; mix SB, with 1.55% naphthalene sulfonate superplasticizer B; and mix SM, with 1.55% melamine sulfonate superplasticizer M. Thus the dosages of melamine sulfonate and naphthalene sulfonate superplasticizers used here are on an equal weight basis, permitting direct comparison of their effects.

7.1 Results

7.1.1 Effects of Superplasticizers on Hydration

Fig. 7.1-1 shows the loss on ignition data vs. time until 24 hours for the pastes SO, SB, and SM, and Fig. 7.1-2 shows the same data of these pastes for times extended to 14 days. All data have been corrected for the ignition loss of the superplasticizer present in the solids. Fig. 7.1-3 shows the results of conduction calorimetry analysis for these three pastes over the first two days. Comparing the calorimetry curve for the admixture-free mix SO and the corresponding previous control mix LO, cement S is confirmed as being slower in hydration than cement L.

The loss of ignition curves for the first day for the two admixture-bearing pastes were similar to each other. The 24-hour data (Fig. 7.1-1) indicated a severe retardation of hydration for both admixture-bearing pastes compared to the control mix SO; between 6 and 24 hours the non-evaporable water contents for both mixes SB and SM were only about one third of that for mix SO.

The retardation effect (reduced non-evaporable water) by the superplasticizer persisted indefinitely (i.e. at least for 14 days) with the naphthalene sulfonate superplasticizer; but with melamine sulfonate superplasticizer it started to diminish after a few days. The loss on ignition value approached that of the control paste at 14 days. Thus the hydration process and resultant products at longer ages appear to be differently affected by the two different superplasticizers.

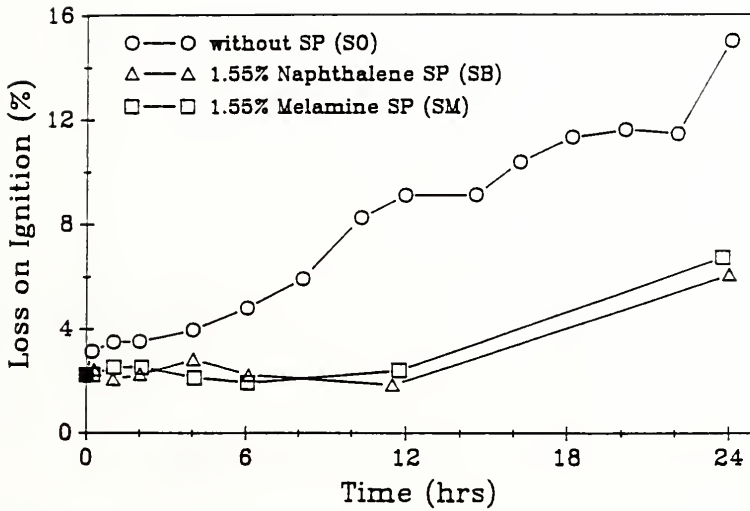


Fig. 7.1-1 Loss on ignition as a function of time up to 1 day for pastes of cement L without superplasticizer (SO), with 1.55% naphthalene sulfonate (SB), and with 1.55% melamine sulfonate (SM)

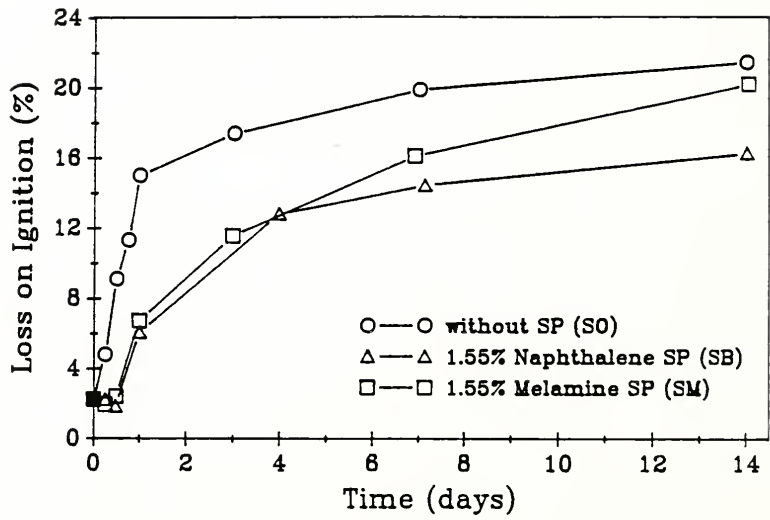


Fig. 7.1-2 Loss on ignition of pastes for periods extended to 14 days

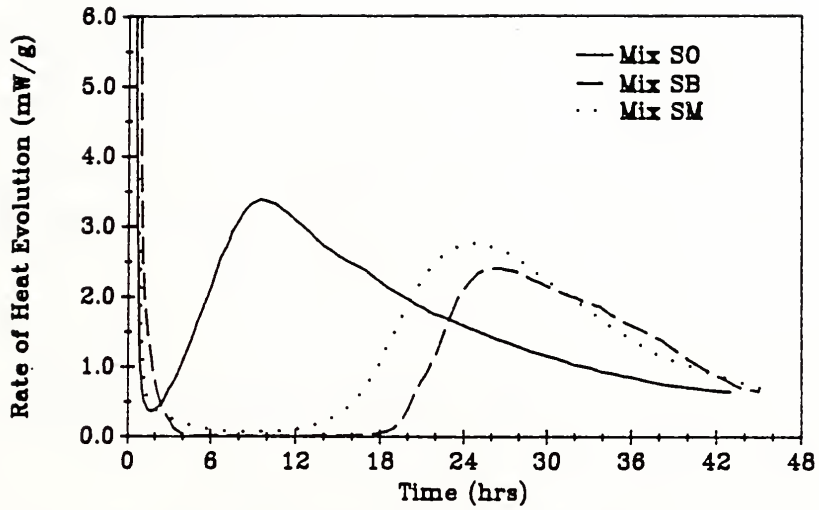


Fig. 7.1-3 Conduction calorimetric curves showing heat evolution vs. time for mixes SO, SB, and SM

From the conduction calorimetry data, the times to peak maximum of the second hydration peak were 7 hours, 21.5 hours, and 22 hours for mixes SO, SB, and SM respectively. Thus both superplasticizers severely retarded hydration; of the two, the melamine sulfonate seems to have slightly less retardation effect.

Fig. 7.1-4 exhibits the mini-slump spread area values as functions of time for these mixes. The pastes with both superplasticizers were entirely fluidized (spread area 1200%), and segregation of the solids and extensive bleeding persisted almost up to set. The kind of segregation observed with the superplasticized pastes was not at all observed for the control pastes. The spread area percentage for the control paste started off only at 450% and steadily diminished with time.

Initial set occurred at 7 hours for the control paste, 19 hours for mix SB, and 20 hours for mix SM. Thus very prolonged delays of the initial set time were produced by both superplasticizers at this very high dosage level.

7.1.2 Control Paste without Superplasticizer (SO): Solution and Solid Phase Analysis

7.1.2.1 Inorganic Ion Concentrations in the Solution Phase

Fig. 7.1-5 shows the concentrations of inorganic ions as functions of time over the first day. The data points between 14 and 22 hours were obtained from a separate run. The inorganic ion concentrations of the pore solution of this cement were generally lower than those for cement L during this 24-hour period.

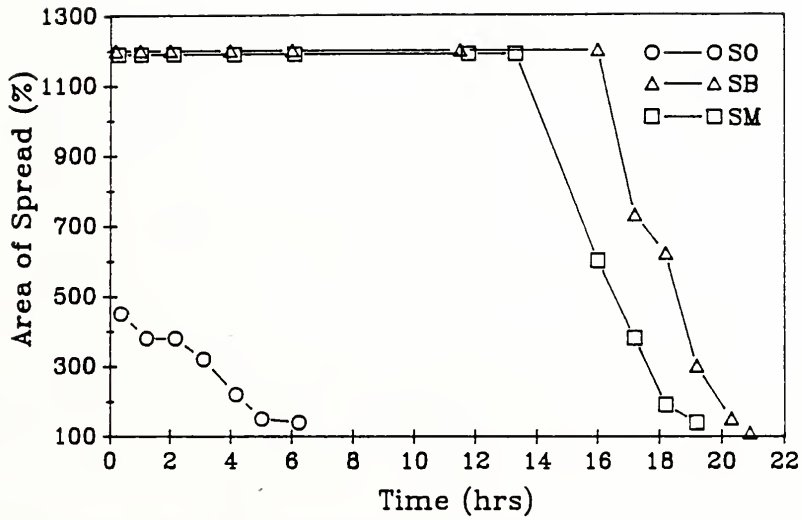


Fig. 7.1-4 Area of spread in mini-slump test vs. time for mixes SO, SB, and SM

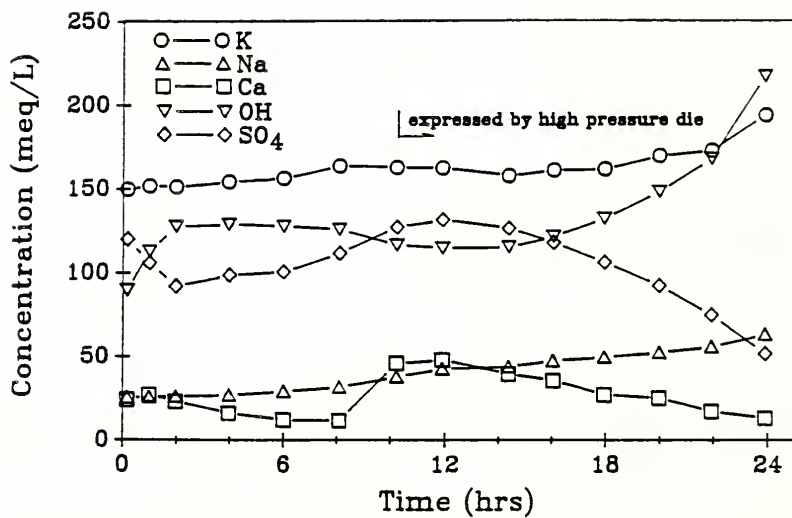


Fig. 7.1-5 Concentration of inorganic ions in mix water and pore solution vs. time in control paste (SO)

The concentrations of the alkali ions, Na^+ and K^+ , were initially at 30 meq/L and 150 meq/L respectively. The Na^+ concentration increased gradually over the first day of hydration. That for K^+ was almost constant for 20 hours or so, then increased somewhat. The concentration of the Ca^{2+} ion was initially at 30 meq/L. It decreased progressively until 8 hours but then it underwent a peculiar jump to a maximum of 50 meq/L before again progressively reducing toward zero.

For the anions, the SO_4^{2-} ion concentration was initially at 120 meq/L. It gradually decreased to a plateau level at around 100 meq/L; subsequently it slightly increased. The maximum concentration was observed at 12 hours. Then the concentration progressively decreased to a residual concentration at 24 hours of around 50 meq/L. The OH^- ion concentration was reasonably stable at 130 meq/L between 1 and 8 hours. Subsequently it first decreased a little then progressively increased, mirroring (in reverse) the sulfate ion concentration changes.

Fig. 7.1-6 provides ion concentration data for this control paste to 14 days. The concentrations of the alkali ions and the OH^- ion rapidly increased between 1 day and 3 days, and continued to increase until 14 days, to a degree greater than the increments of the corresponding ions observed for cement L. At 14 days, the OH^- ion concentration was around 500 meq/L; for cement L, it was 470 meq/L. The Ca^{2+} and SO_4^{2-} ions were absent from the pore solution in pastes older than 3 days.

Table 7.1-1 shows the sum of the cation concentrations and the sum of the anion concentrations and its balance for the control paste SO. Until the age of 8 hours, 10 to

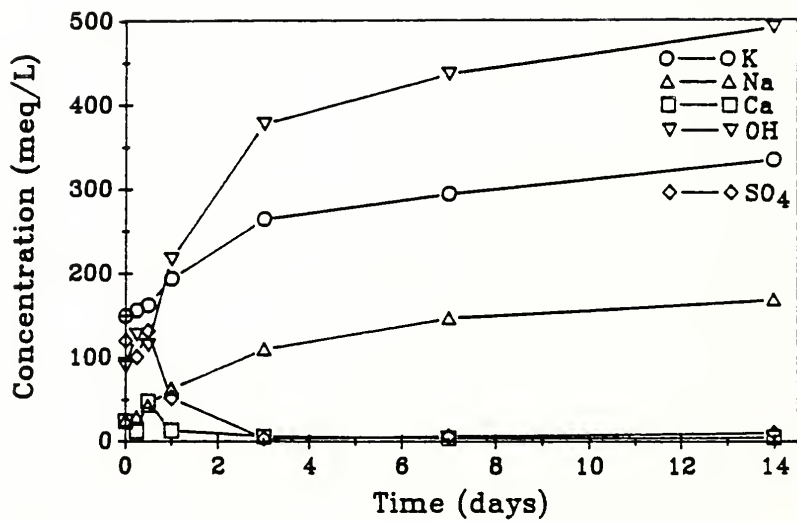


Fig. 7.1-6 Concentration of inorganic ions in pore solution vs. time for extended periods up to 14 days in control paste (SO)

Table 7.1-1 Experimental cation-anion balance in solution for mix SO

Age	Σ Cations (meq/L)	Σ Anions (meq/L)	Difference (meq/L)
(hr)			
0.17	198.8	209.3	- 10.5
0.98	204.3	218.3	- 14.1
1.97	200.2	219.4	- 19.2
3.97	197.2	227.6	- 30.4
6.00	197.4	228.1	- 30.7
8.08	206.9	237.2	- 30.3
10.23	246.4	243.4	+ 3.0
11.90	252.9	246.1	+ 6.9
14.37	241.0	242.7	- 1.7
16.05	243.8	240.8	+ 3.1
17.95	238.2	240.1	- 1.9
19.97	247.1	242.6	+ 4.4
21.92	245.4	245.3	+ 0.1
23.90	269.9	268.5	+ 1.4
(day)			
3.00	380.5	381.1	- 0.7
7.00	445.4	446.3	- 0.9
13.98	508.6	503.2	+ 5.5

30 meq/L excess of anions are observed; this excess is larger than the numbers observed for the control paste of cement L. The anion-cation balances are more nearly equal for the rest of the hydration period.

7.1.2.2 Solid Phase Analyses

Fig. 7.1-7 presents the results of analyses of CaSO_4 -bearing compounds in the solid phase for the control pastes SO, as functions of time for the first 24 hours. The initial form of CaSO_4 in the cement S was a mixture of hemihydrate and gypsum. Those two hydrated forms of CaSO_4 and ettringite were quantified by the DSC analysis. Again, the quantities of the CaSO_4 -bearing compounds are expressed in terms of equivalent % SO_4 of the compound analyzed, based on the ignited weight of the pastes.

The initial SO_4 content in cement S was 1.5% SO_4 as hemihydrate and 0.8% SO_4 as gypsum. The rate of dissolution of hemihydrate and conversion to gypsum was quick, and no hemihydrate was detected in even the first hydrated cement paste sample. The observed gypsum content at 10 minutes was 1.8% SO_4 equivalent; this reflects the sum of residual original gypsum plus secondary gypsum produced immediately from the hemihydrate. The gypsum content remained at around this level until about 4 hours. It was then gradually consumed, diminishing to zero by 16 hours.

The observed ettringite content rose immediately to 0.8% SO_4 equivalent at 10 minutes. Then the ettringite formed increased progressively to about 1.7% SO_4

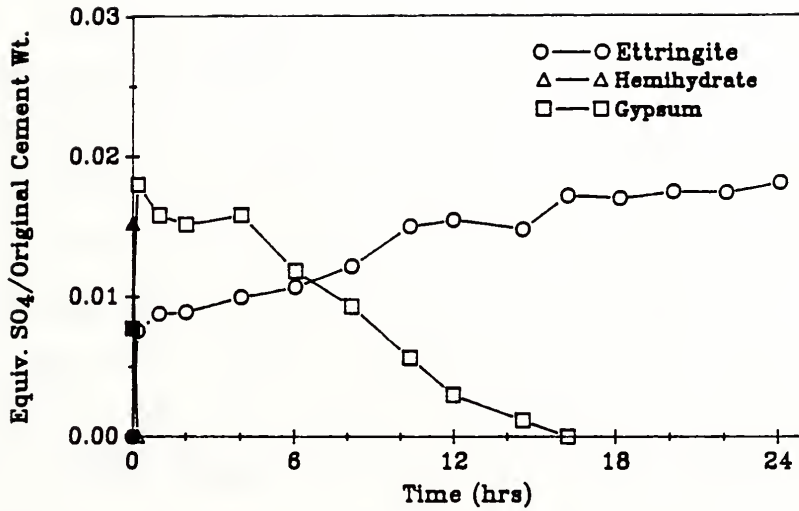


Fig. 7.1-7 Content of sulfate-bearing phases in paste solids vs. time up to 1 day for control paste SO
(Percentage of each solid phase re-expressed in terms of its SO_4 content.)

equivalent at 24 hours.

This time-dependent pattern of the solid phases for cement S reflects a milder sulfate response than with the cement L. Both gypsum consumption and ettringite formation were not so abrupt.

Fig. 7.1-8 show the same patterns extended to 14 days. No calcium monosulfaluminate hydrate was detected by DSC during this period, and the ettringite content seems to be approximately constant. The actual DSC curves for specimens at 1 day and older are shown in Fig. 7.1-9.

The characteristic dehydration peak of ettringite was less sharp for the control paste SO than for the corresponding control paste LO. The ettringite peaks exhibited here are in the broad range between 40° and 110°C. Again the exact boundaries of the peaks are difficult to document with certainty. The two extensions of the baseline shown in the figure as bounding the area of dehydration peak represent the approximate minimum and maximum possibilities in each case. A representative value was selected in the middle of those, as explained in the previous chapter. The possible variation in ettringite content between the extremes was about 10%.

Table 7.1-2 shows the observed balance of sulfate-bearing forms in this paste as a function of time. The total sulfate content of cement S according to the mill analysis is equivalent to 3.36% as SO_4 . In the cement itself, the sum of the sulfates accounted for by these analytical methods was only 2.2%; obviously some of the sulfate, such as alkali or alkali calcium sulfate or any soluble anhydrite present were not included in

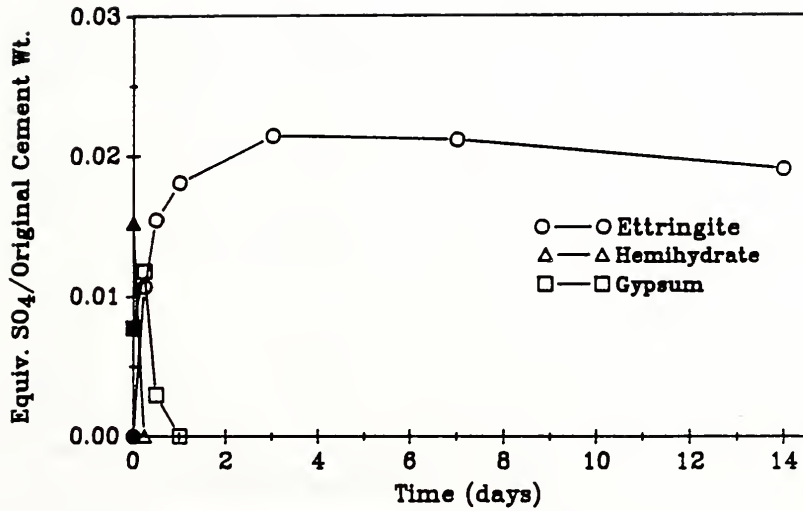


Fig. 7.1-8 Content of sulfate-bearing phases in paste solids vs. time for extended periods up to 14 days for control paste SO

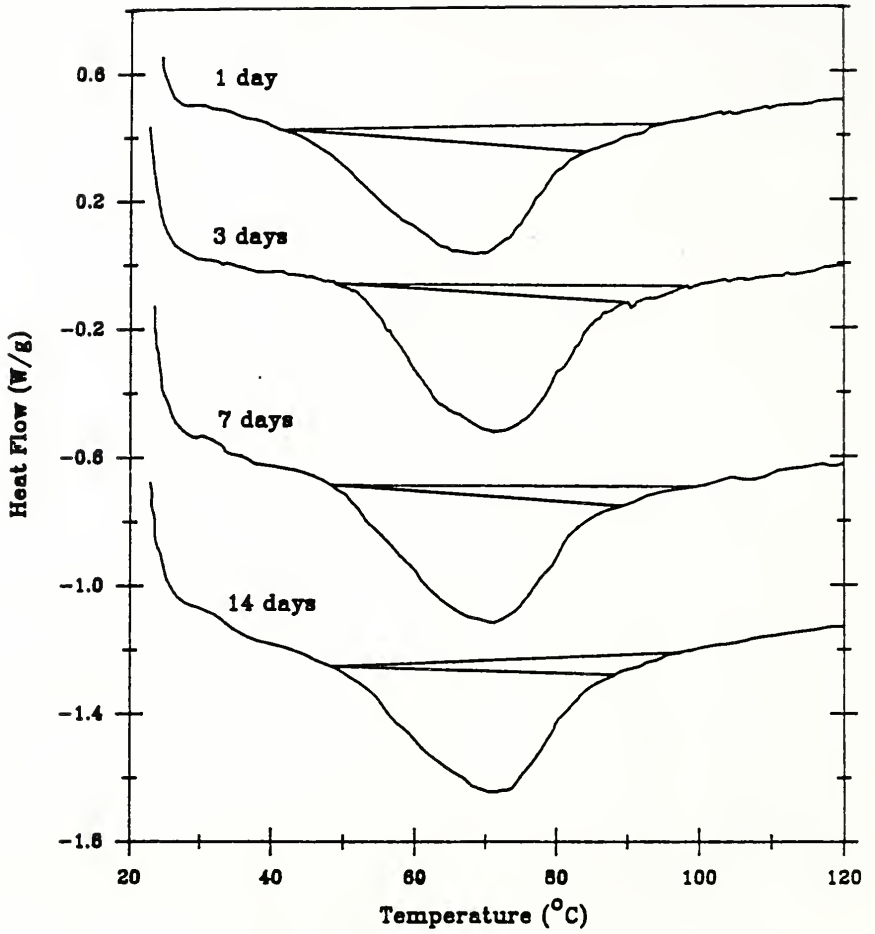


Fig. 7.1-9 DSC curves of the control paste samples at 1 day to 14 days

Table 7.1-2 Total balance of sulfate-bearing phase for mix SO

(Percentages expressed in terms of equivalent SO_4 content)

Age (hr)	Hemihydrate (%)	Gypsum (%)	Ettringite (%)	Σ Solid (%)	Solution (%)	Total (%)
0.00	1.52	0.77	0.00	2.29	0.00	2.29
0.22	0.00	1.80	0.75	2.55	0.29	2.84
1.02	0.00	1.58	0.88	2.46	0.25	2.71
2.00	0.00	1.51	0.89	2.40	0.22	2.62
4.02	0.00	1.58	1.00	2.58	0.24	2.81
6.03	0.00	1.18	1.07	2.25	0.24	2.49
8.15	0.00	0.93	1.22	2.15	0.27	2.42
10.33	0.00	0.56	1.50	2.06	0.31	2.37
11.97	0.00	0.30	1.54	1.84	0.32	2.16
14.57	0.00	0.12	1.48	1.60	0.31	1.90
16.23	0.00	0.00	1.72	1.72	0.29	2.00
18.17	0.00	0.00	1.70	1.70	0.26	1.96
20.13	0.00	0.00	1.75	1.75	0.23	1.97
22.10	0.00	0.00	1.74	1.74	0.19	1.93
24.10	0.00	0.00	1.81	1.81	0.12	1.93
(day)						
3.02	0.00	0.00	2.14	2.14	0.01	2.15
7.01	0.00	0.00	2.12	2.12	0.02	2.14
14.01	0.00	0.00	1.91	1.91	0.03	1.93

* The total SO_4 content of the cement by the mill analyses was 3.36% as SO_4 .

the analysis. After the hydration started, the sum of the analyzed sulfates (including the SO_4^{2-} ion in solution) increased to about 2.7% between 0.2 and 4 hours, and then it decreased to about 2%. After one day, the data showed some scatter. The progressive reduction with time in this parameter was attributed to incorporation of sulfate in increasing amounts in the C-S-H gel as it developed over time.

The SO_4^{2-} ion concentration in the paste solution reached a maximum and then decreased when the solid gypsum was almost exhausted around 12 to 14 hours. It is thus again confirmed that the solid gypsum controls the sulfate ion in the early pore solution.

7.1.3 Paste with Naphthalene Sulfonate Superplasticizer B (SB): Solution and Solid Phase Analysis

7.1.3.1 Removal of Superplasticizer from Solution

Fig. 7.1-10 indicates the concentration of naphthalene sulfonate superplasticizer B remaining in solution as a function of time until 24 hours, and the same plot is extended to 14 days in Fig. 7.1-11. The amount of the superplasticizer removed from solution immediately by the cement was approximately one half of the initial concentration. This is larger than the amount of naphthalene sulfonate initially removed by cement L.

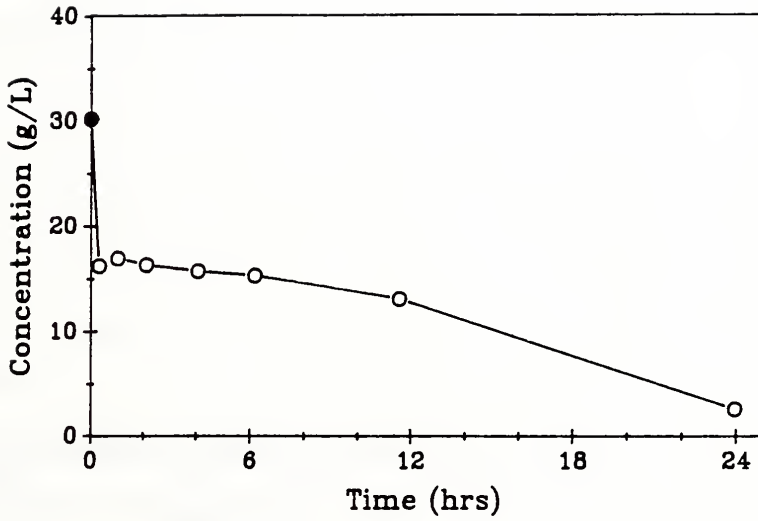


Fig. 7.1-10 Concentration of residual superplasticizer in mix water and pore solution for naphthalene sulfonate bearing pastes (SB) up to 1 day

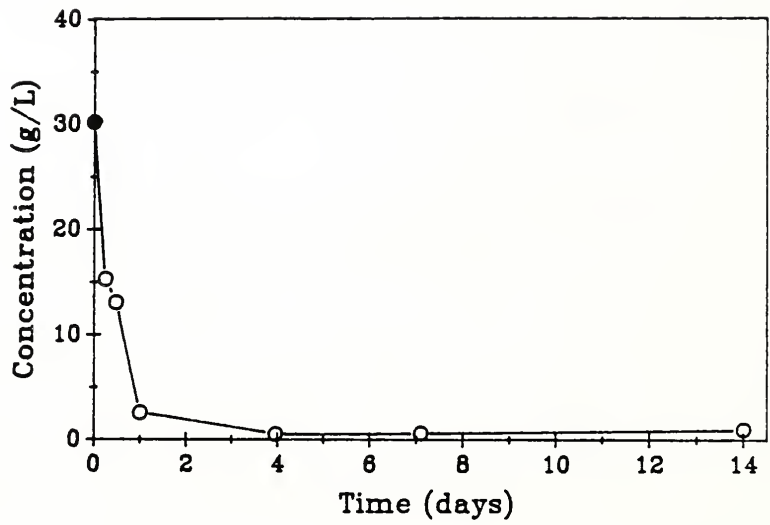


Fig. 7.1-11 Concentration of residual superplasticizer in pore solution of SB pastes for extended periods up to 14 days

The superplasticizer concentration in solution decreased slowly for a time up to 12 hours, and more drastically between 12 and 24 hours, to a residual concentration of about 3 meq/L. This low residual concentration did not change thereafter.

7.1.3.2 Inorganic Ion Concentrations in the Solution Phase

Fig. 7.1-12 shows the changes in inorganic ion concentrations up to 24 hours for the mix SB. Reflecting the slow hydration of this cement and the severe retardation effect of the admixture, the inorganic ions concentrations changed only slightly over the first day of hydration.

The Na^+ ion concentration was initially 120 meq/L. It increased quickly to 150 meq/L and maintained this approximate level for 24 hours. The corresponding level for the SO paste was only 120 meq/L. The K^+ ion concentration here stayed at around 140 meq/L, slightly lower than the control case. The concentration level of the Ca^{2+} ion increased during the first few hours to 70 meq/L. The concentration-time pattern for Ca^{2+} here is much different from that of the control SO paste, and the level was generally higher; it stayed up at 40 meq/L even at 24 hours.

With respect to anions, much of the sulfate was immediately dissolved, and SO_4^{2-} reached a concentration of 170 meq/L at 10 minutes, much higher than the control samples. It decreased to 120 meq/L over the next 4 hours, and then increased again. Its concentration was always higher than the control paste during this period. Even at 24 hours, it was still as high as 150 meq/L.

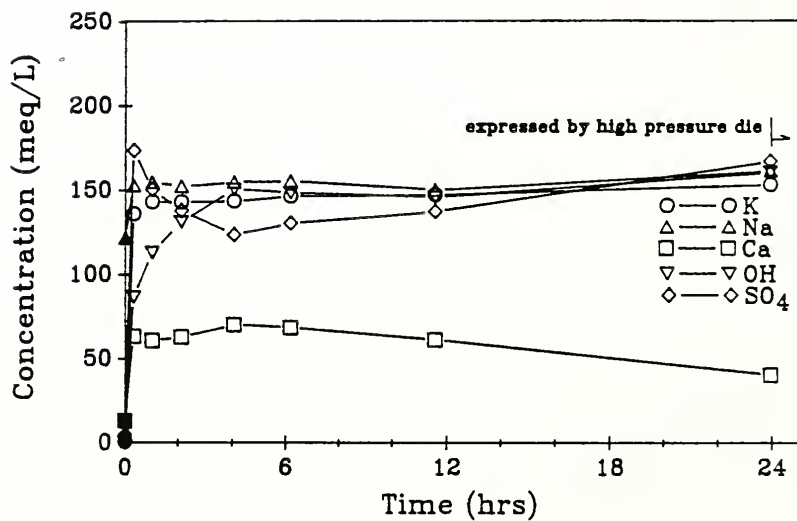


Fig. 7.1-12 Concentration of inorganic ions in mix water and pore solution vs. time in paste with naphthalene sulfonate superplasticizer (SB)

The OH^- ion concentration increased gradually in the first 4 hours, and then stabilized at about 150 meq/L until 24 hours. Unlike the control case, no progressive increase in concentration was observed in this period.

Fig. 7.1-13 shows the same concentration patterns until 14 days. The Ca^{2+} and SO_4^{2-} concentrations had dropped to almost zero by 4 days. Again the alkali ions and the OH^- ion increased markedly between 1 day and 4 days, and only slightly thereafter. During the period from 4 to 14 days, the K^+ concentration was about 40 meq/L lower and the Na^+ concentration was higher by about 120 meq/L, than those of the control mix. The OH^- ion concentration was higher by 50 meq/L than the control mix SO at 14 days. These longer-term elevations of sodium ion concentration and corresponding OH^- ion concentration as a result of the addition of the naphthalene sulfonate, were seen to be similar to those produced with cement L.

Table 7.1-3 shows that the sum of inorganic cations and anions and their balance along with analyses on the residual polymer concentrations. The charge density for the naphthalene sulfonate polymer still in solution was calculated in the same way as was previously done for cement L.

In general, the results seemed similar to those for the mix LB, and the same analytical procedure on the polymer anions seemed to be applicable. The excess of cations balancing the residual polymer anions was seen at each age. The excess of cations was obviously very highly correlated with the residual polymer content for the first 12 hours, as indicated by the virtual constancy of the calculated charge density

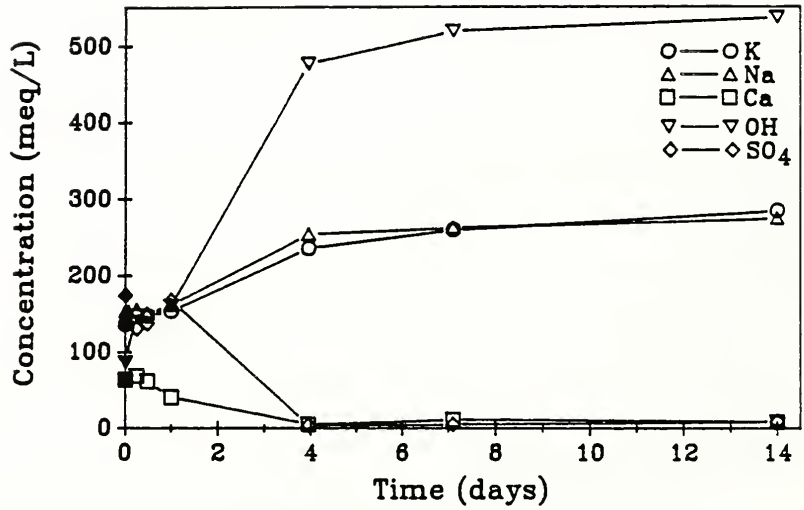


Fig. 7.1-13 Concentration of inorganic ions in pore solutions of naphthalene sulfonate bearing pastes (SB) vs. time for extended periods up to 14 days

Table 7.1-3 Experimental cation-anion balance in solution for mix SB

Age (hr)	Σ Cations (meq/L)	Σ Inorganic Anions (meq/L)	Difference (meq/L)	Polymer Conc. (g/L)	Calculated Charge Density* (meq/g)
0.00	134.8	5.7	+ 129.1	32.2	4.01
0.33	352.1	260.2	+ 92.0	17.3	5.32
1.03	358.3	264.4	+ 93.9	18.0	5.20
2.12	357.9	270.6	+ 87.3	17.4	5.03
4.07	368.3	276.3	+ 92.0	16.7	5.50
6.18	369.9	280.7	+ 89.2	16.3	5.48
11.57	358.2	284.7	+ 73.5	13.9	5.29
23.95	354.9	328.1	+ 26.8	2.7	(9.82)
(day)					
3.95	494.2	481.9	+ 12.3	0.6	(21.85)
7.10	533.3	525.4	+ 7.9	0.7	(11.86)
14.00	566.5	546.5	+ 20.0	1.0	(19.10)

* of residual superplasticizers in solution.

offered as the ratio of these two parameters. However for 24 hours and later, the calculated charge density became large and inconsistent, due to the very small residual concentrations of the polymer at long ages.

As discussed in section 6.2.1, the calculated charge density at time zero, i.e. in the mix water before cement has been added, was 4 meq/g, lower than those in the paste liquids between the start of hydration and 12 hours. These are reasonably constant at about 5.30 meq/g. Thus from the observation in both mixes LB and SB, the naphthalene sulfonate polymers in the mix water, and that fraction of them that remains unadsorbed in the paste solutions in the early hours have different values of charge density.

7.1.3.3 Solid Phase Analyses

Fig. 7.1-14 shows the results of the CaSO_4 -bearing phases determined for paste SB (with 1.55% naphthalene sulfonate superplasticizer) for the first day of hydration.

The heavy dosage of the superplasticizer B again resulted in severe retardation, as had been seen previously for mix LB. In the present results, the gypsum content for the first few hours was more constant, and the ettringite production rate was slowed down compared to the control mix data previously shown in Fig. 7.1-7. Here the content of the gypsum was almost constant for the first 6 hours at 0.9% SO_4 equivalent, a lower level than the control case. It then decreased, and reached zero probably a little earlier than the 24 hours shown in the plot (no data being taken between 12 and 24

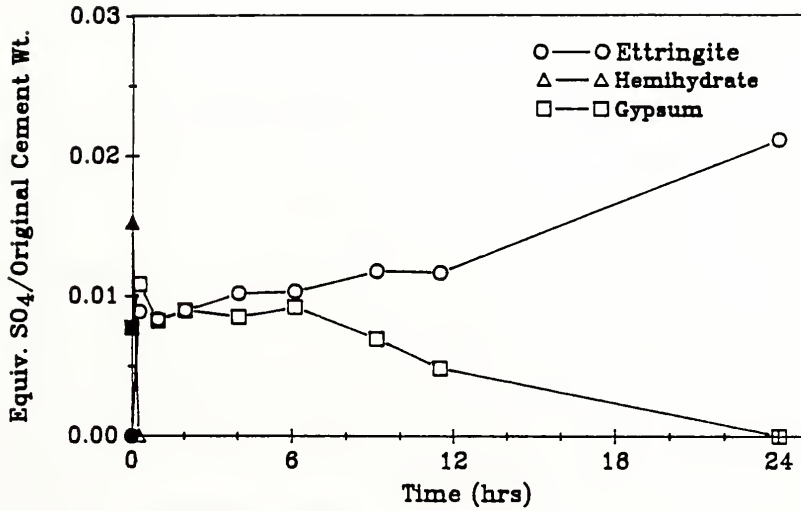


Fig. 7.1-14 Content of sulfate-bearing phases found in paste solids vs. time up to 1 day for naphthalene sulfonate bearing pastes (SB)
(Percentage of each solid phase re-expressed in terms of its SO_4 content.)

hours). At 24 hours, the sulfate ion concentration in the pore solution was still in the period of the "plateau" level before the sudden drop.

The ettringite content here was also almost constant for the first 12 hours at a comparatively low value of 0.9% SO_4 equivalent; however, it had increased to well over 2% SO_4 by 24 hours.

Fig. 7.1-15 shows the same patterns as Fig. 7.1-14 in the longer term until 14 days. The results of two replicate runs on different days are plotted. One of the points (at 4 days) in the first run was low, and is assumed to have been a deviant point and is not shown.

Again no calcium aluminate monosulfate hydrate was detected throughout the period of study. However, the ettringite content determination for this mix SB samples was subject to a different kind of complication. As is seen for example in Fig. 7.1-16, at one day the dehydration peak in the DSC curve has a complicated geometry at the higher temperature side. Three different inflection points are observed, two of which are points at which the derivative changes from higher to lower values, and an intermediate one at which the derivative changes from lower to higher values. The latter is not reasonable as a possible baseline-defining point. However, if the lower temperature higher to lower derivative inflection point were used as a baseline-defining point, the area included within the ettringite peak would be obviously too small. Thus the highest temperature inflection point was used as a baseline-defining point, as shown in the figure. This phenomenon was not observed for the paste LB.

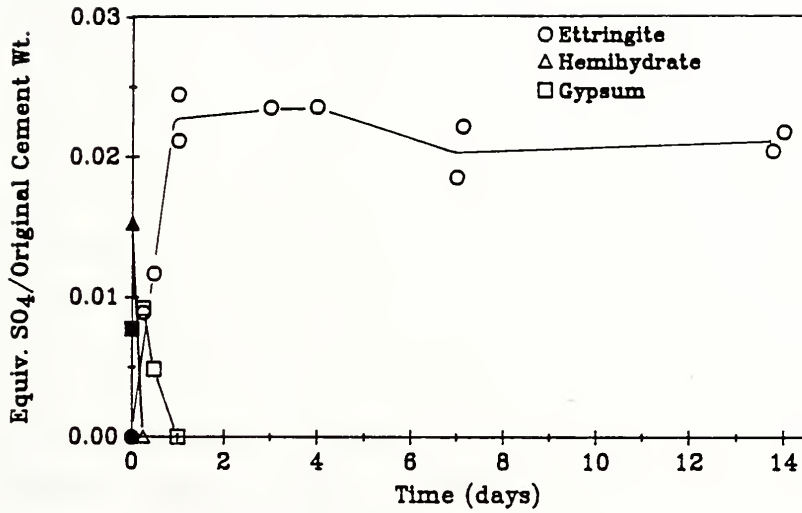


Fig. 7.1-15 Content of sulfate-bearing phases found in paste solids vs. time up to 14 day for naphthalene sulfonate bearing pastes (SB)

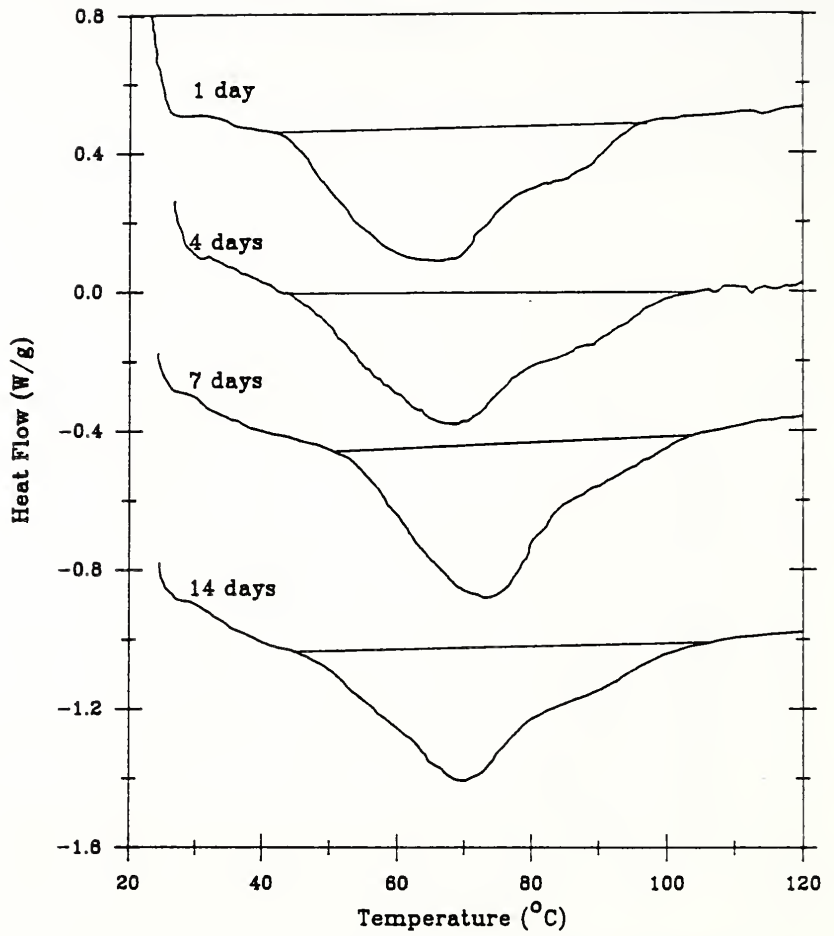


Fig. 7.1-16 DSC curves of the paste SB samples at 1 day to 14 days

This phenomenon is believed to represent a shift in the dehydration process, i.e. a shoulder caused by the incorporation of the superplasticizer on or within AFt compounds. There was no sulfate-bearing compound other than ettringite detected in XRD, and the low hump indicative of C_4AH_{13} was the same in intensity as seen previously in the control paste. Judging from the height of the XRD peak for ettringite, the amount of ettringite present at each age appeared to be in the same order as for the mix LB. From these indications, it appears that the proper end point of the ettringite dehydration peak was the one selected as indicated in Fig. 7.1-16.

The trend of ettringite content observed for samples older than one day seemed to indicate that ettringite was constant at about 2.2% SO_4 equivalent.

A shoulder similar to the shoulder on the DSC peak for ettringite was also observed on the corresponding DSC peak for gypsum in these naphthalene sulfonate-treated pastes. This shoulder may reflect the absorption of naphthalene sulfonate polymer on the surfaces of the gypsum crystals. Fig. 7.1-17 shows this effect.

Table 7.1-4 shows the balance in terms of sulfate for the mix SB. The total sulfate for the superplasticized paste was quite constant at a little over 2% SO_4 equivalent consistently over the 14 day period. The general level was lower than that for the control mix. As was reasoned similarly in the corresponding mix with cement L, with superplasticizer present, much of the sulfate appears to be present in phases not accounted for in the calculation.

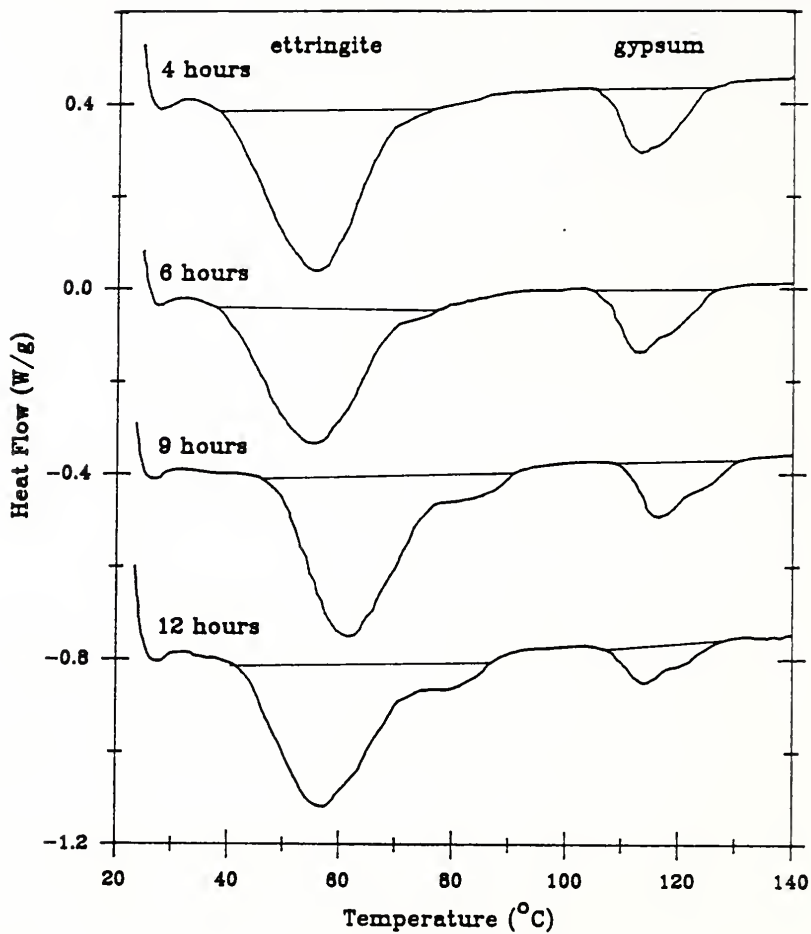


Fig. 7.1-17 DSC curves of the paste SB samples at 4 hour to 12 hours

Table 7.1-4 Total balance of sulfate-bearing phase for mix SB

(Percentages expressed in terms of equivalent SO_4 content)

Age (hr)	Hemihydrate (%)	Gypsum (%)	Ettringite (%)	Σ Solid (%)	Solution (%)	Total (%)
0.00	1.52	0.77	0.00	2.29	0.01	2.30
0.30	0.00	1.09	0.89	1.97	0.42	2.39
1.00	0.00	0.82	0.83	1.65	0.36	2.01
2.02	0.00	0.90	0.90	1.80	0.33	2.13
4.03	0.00	0.85	1.02	1.87	0.30	2.17
6.10	0.00	0.92	0.89	1.81	0.31	2.12
11.50	0.00	0.48	1.17	1.65	0.33	1.98
24.02	0.00	0.00	2.11	2.11	0.40	2.51
(day)						
3.99	0.00	0.00	2.31	2.31	0.01	2.32
7.14	0.00	0.00	2.21	2.21	0.01	2.22
14.02	0.00	0.00	2.17	2.17	0.02	2.19

7.1.4 Paste with Melamine Sulfonate Superplasticizer M (SM): Solution and Solid Phase Analysis

7.1.4.1 Removal of Superplasticizer from Solution

Fig. 7.1-18 illustrates the concentration of the melamine sulfonate superplasticizer M remaining in solution as a function of time until 24 hours in paste of cement S treated with 1.55% by weight of melamine sulfonate superplasticizer. The initial dosage here is the same 1.55% as for the naphthalene sulfonate admixtures in the pastes SB, so that the results are directly comparable. The absorption pattern was quite similar to that for the mix SB (shown by a dotted line in the same figure), except that the transient concentration of melamine sulfonate was about 3g/L lower than that of naphthalene sulfonate between 1 and 12 hours. After one day, the pattern was identical to the mix SB as only a trace amount remained in solution, as seen in Fig. 7.1-19.

7.1.4.2 Inorganic Ion Concentrations in the Solution Phase

Fig. 7.1-20 shows concentrations of inorganic ions found for the mix SM. The patterns for the first 24 hours look very similar to those for the corresponding naphthalene sulfonate-bearing paste SB, shown in Fig. 7.1-12.

Here again the Na^+ ion and the K^+ ion concentrations were stabilized in the 160-170 meq/L range (Na^+) and at 150 meq/L (K^+), both levels are almost equal to those for the paste SB. Here the Ca^{2+} jumped to 100 meq/L at the first measurement,

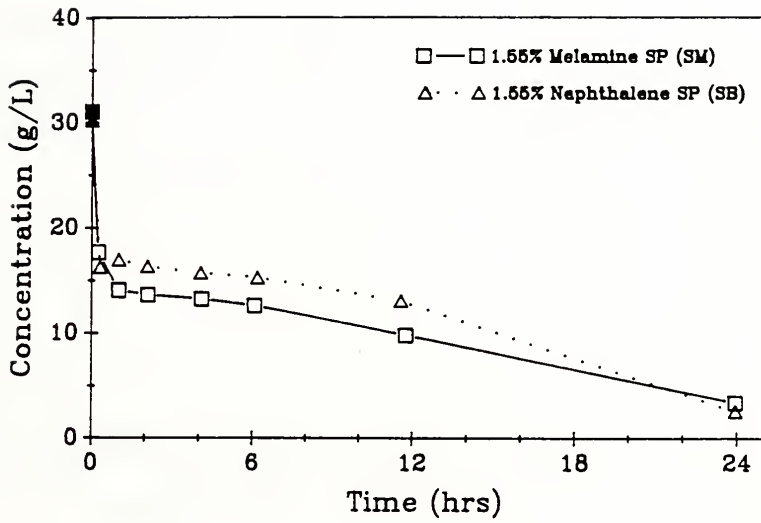


Fig. 7.1-18 Concentration of residual superplasticizer in mix water and pore solution for melamine sulfonate bearing pastes (SM) up to 1 day

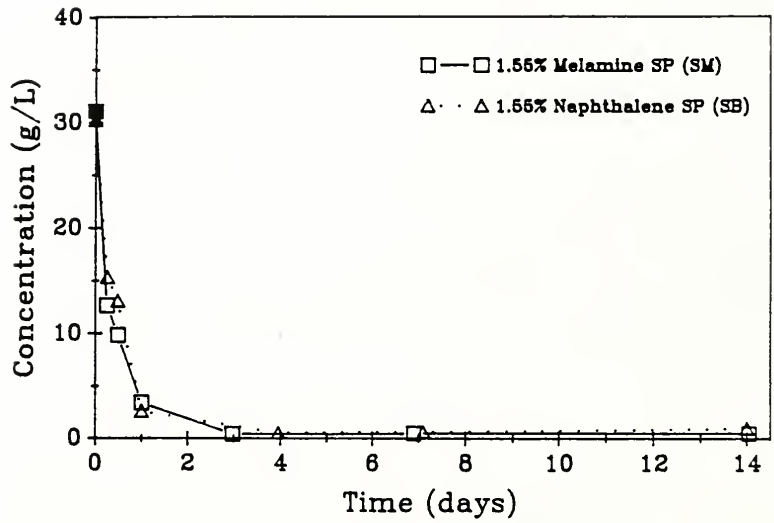


Fig. 7.1-19 Concentration of residual superplasticizer in pore solution of SM pastes for extended periods up to 14 days

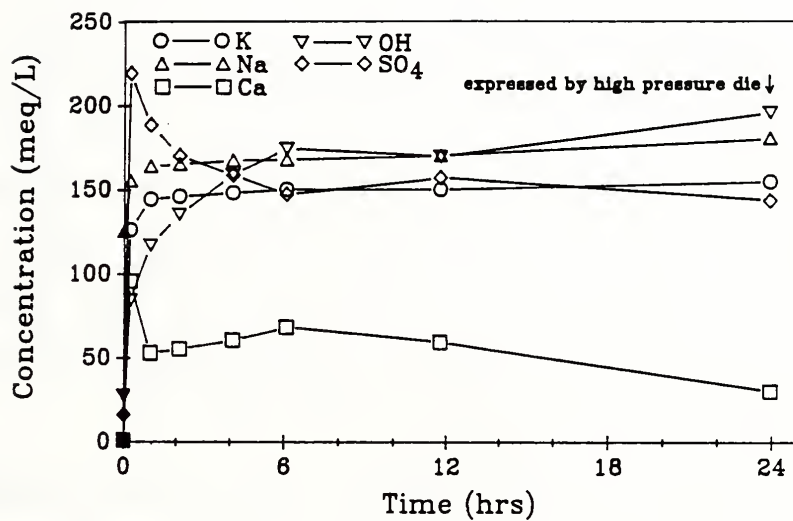


Fig. 7.1-20 Concentration of inorganic ions in mix water and pore solution vs. time in paste with melamine sulfonate superplasticizer (SM)

but then it went back to a constant level at around 50 meq/L and decreased to 30 meq/L between 12 and 24 hours, also considerably higher than the control paste.

The patterns for the SO_4^{2-} ion was similar to that found for the mix SB but the concentration level was a little higher. The initial concentration was as high as 220 meq/L and went down gradually to a plateau at 150 meq/L which maintained for 24 hours. The OH^- ion concentration plateaued at 170 meq/L, a little higher than the mix SB, in the first 6 hours. Again there was no sudden increase in concentration during the first 24 hours of hydration.

Fig. 7.1-21 shows the same data extended to 14 days for the mix SM. Again these are very similar to those for the paste SB. A few differences are that the OH^- ion and the K^+ ion concentration were slightly higher than those for the mix SB. The OH^- ion concentration here was about 580 meq/L at 14 days, 50 meq/L higher than the paste SB, and 100 meq/L higher than the control paste. For the K^+ ion, its concentration level up to 14 days was almost same as that of the control paste, around 300 meq/L at 14 days.

Table 7.1-5 shows the same calculations of the charge balance as Table 7.1-3 for the paste SM. This analysis of polymer anion seems to be also applicable to the melamine sulfonate superplasticizer. The correlation of the two parameters, the excess of the cations and the polymer concentration in pore solution, were significant. However, the concentration is not quite as exact as was the case for naphthalene sulfonate superplasticizer, as can be seen from the variation in the calculated charge den-

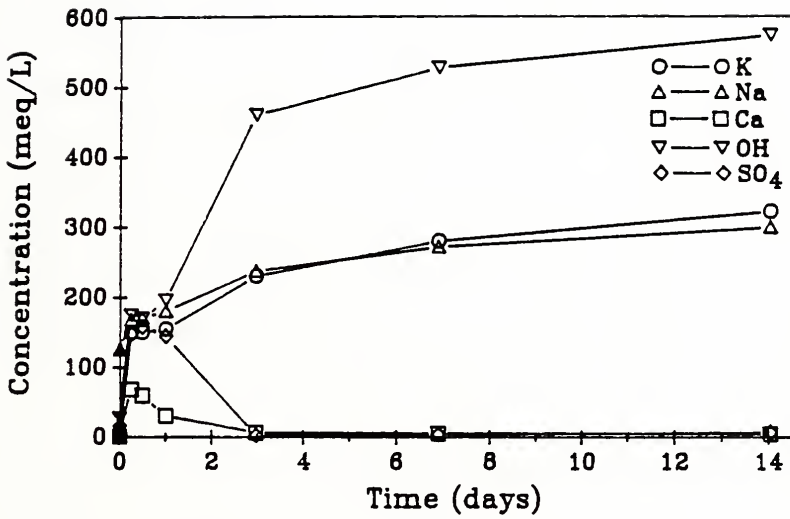


Fig. 7.1-21 Concentration of inorganic ions in pore solutions of melamine sulfonate bearing pastes (SM) vs. time for extended periods up to 14 days

Table 7.1-5 Experimental cation-anion balance in solution for mix SM

Age (hr)	Σ Cations (meq/L)	Σ Inorganic Anions (meq/L)	Difference (meq/L)	Polymer Conc. (g/L)	Calculated Charge Density* (meq/g)
0.00	127.8	43.6	+ 84.2	31.0	2.71
0.27	377.4	309.0	+ 68.4	17.6	3.88
1.03	361.4	304.6	+ 56.8	14.0	4.05
2.12	367.0	305.3	+ 61.7	13.6	4.53
4.10	376.4	318.2	+ 58.2	13.2	4.40
6.08	386.6	322.6	+ 64.1	12.6	5.09
11.77	380.3	327.5	+ 52.8	9.8	5.39
23.95	365.7	340.6	+ 25.1	3.4	(7.48)
(day)					
2.97	474.6	463.2	+ 11.4	0.4	(26.94)
6.89	557.7	531.9	+ 25.8	0.5	(51.54)
14.04	626.8	581.3	+ 45.5	0.5	(95.42)

* of residual superplasticizers in solution.

sity. The overall calculated charge density of the polymer before absorption was less than 3 meq/g. For the cement paste solutions, it progressively increased; to about 4 meq/g at 15 minutes, and to more than 5 meq/g by 12 hours. The calculated charge density values at later ages were considered to be unrealistic due to the very small values of the residual concentration used as the denominator in the calculation.

7.1.4.3 Solid Phase Analyses

Fig. 7.1-22 shows the patterns of CaSO_4 -bearing phases for the mix SM up to 1 day. Generally, the results were analogous to the paste with naphthalene sulfonate superplasticizer. Again no calcium aluminate monosulfate hydrate was observed for the whole period. Hemihydrate was still detected at 16 minutes, but it was dissolved or converted to gypsum before 1 hour. The pattern for the gypsum content was similar in its magnitude and duration to that for the paste SB. The maximum formation of gypsum occurred at 1 hour and the content was 0.9% equivalent of SO_4 , which was lower than the control paste. The gypsum content was constant around 0.6% from 4 to 12 hours, and it was entirely consumed sometime before 24 hours.

The pattern for ettringite was a little different either from that for the paste SB or the control paste SO. The ettringite content increased to 1.3% as equivalent SO_4 at 1 hour, but then remained almost constant until 12 hours. This quantity was the highest of three pastes of cement S, for the first 6 hours. Between 12 and 24 hours, ettringite increased significantly to 2.2% equivalent SO_4 , which was higher than the control mix.

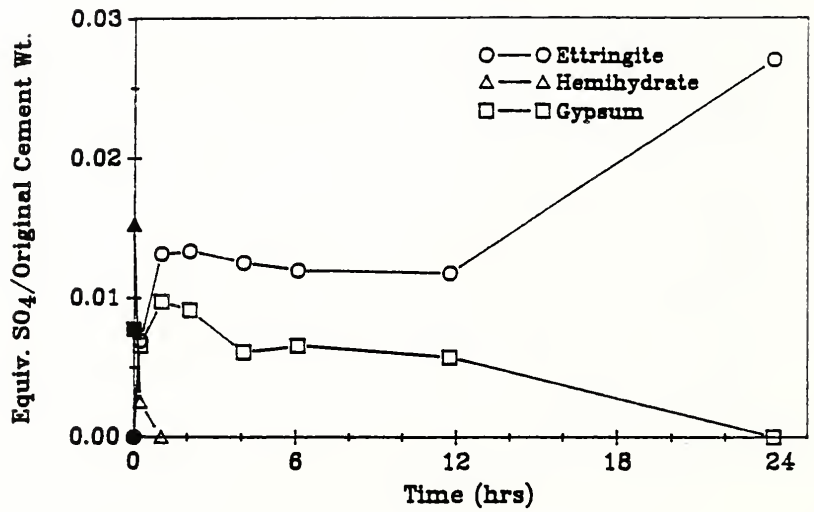


Fig. 7.1-22 Content of sulfate-bearing phases found in paste solids vs. time up to 1 day for melamine sulfonate bearing pastes (SM)
(Percentage of each solid phase re-expressed in terms of its SO₄ content.)

Fig. 7.1-23 is the same figure extended up to 14 days. There is an apparent downward trend on the ettringite content from 1 day to 7 days, followed by an apparent stabilization in ettringite content at about 2.5% SO_4 equivalent. No compounds other than ettringite that are considered to incorporate Ca and SO_4 were detected by XRD analysis. As mentioned in the section concerning the solid phases analysis of the paste SB, determination of the ettringite content by DSC for the samples after one day are subject to a complication associated with the shoulder of its dehydration peak. As shown in Fig. 7.1-24, the same complication exists here. The results of two replicate runs on different days are presented on the figure. One of the points at 14 days seemed unreasonable and was not included in the analysis. The same method for the baseline determination as the paste SB was also applied here, i.e. the shoulder was included.

The ettringite contents determined here are very much larger than for the control paste and the paste SB, which were only of the order of about 2.1% SO_4 equivalent.

Table 7.1-6 shows the combined data of all the CaSO_4 -bearing phases determined over the 14 days period for paste SB. The sum of the total solid sulfate phases and the sulfate ion in solution was high at around 2.7% for 1 and 2 hours; it decreased to approximately 2.2% SO_4 equivalent before increasing again at ages of 1 day and later.

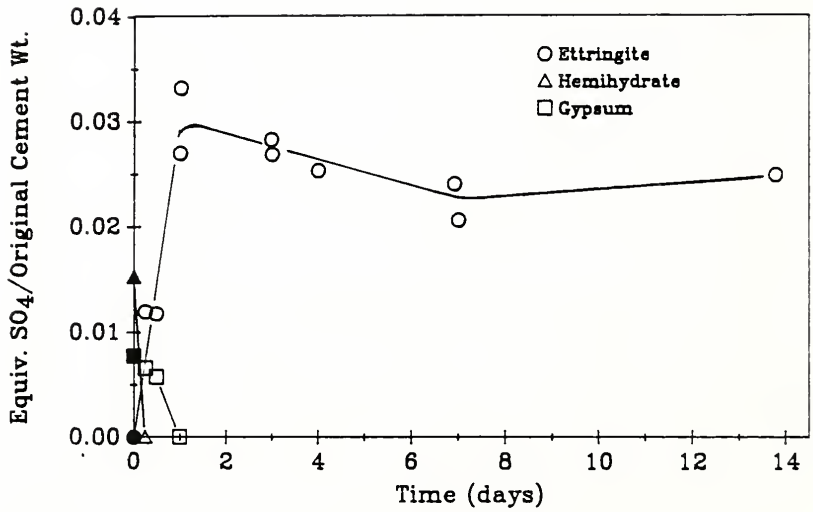


Fig. 7.1-23 Content of sulfate-bearing phases found in paste solids vs. time up to 14 day for melamine sulfonate bearing pastes (SM)

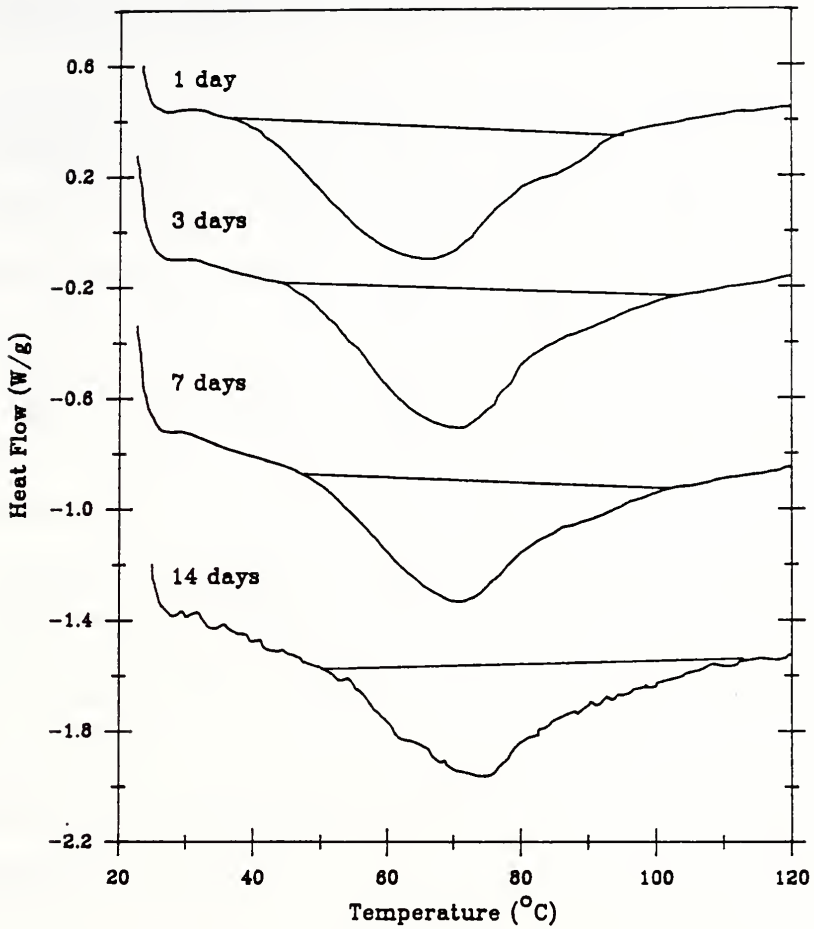


Fig. 7.1-24 DSC curves of the paste SM samples at 1 day to 14 days

Table 7.1-6 Total balance of sulfate-bearing phase for mix SM

(Percentages expressed in terms of equivalent SO_4 content)

Age (hr)	Hemihydrate (%)	Gypsum (%)	Ettringite (%)	Σ Solid (%)	Solution (%)	Total (%)
0.00	1.52	0.77	0.00	2.29	0.04	2.33
0.25	0.25	0.66	0.69	1.60	0.54	2.13
1.03	0.00	0.97	1.31	2.28	0.45	2.74
2.08	0.00	0.91	1.33	2.24	0.41	2.65
4.07	0.00	0.61	1.25	1.86	0.38	2.24
6.07	0.00	0.66	1.19	1.85	0.36	2.21
11.75	0.00	0.57	1.17	1.74	0.38	2.12
23.77	0.00	0.00	2.70	2.70	0.35	3.05
(day)						
2.99	0.00	0.00	2.83	2.83	0.01	2.84
6.91	0.00	0.00	2.40	2.40	0.01	2.41
14.06	0.00	0.00	2.50	2.50	0.02	2.52

7.2 Discussion

7.2.1 Characteristics of Removal of Naphthalene Sulfonate Superplasticizers from Solution by the Two Gray Cements

The initial removal of the naphthalene sulfonate superplasticizer from solution by cement S was greater than that by cement L. Many factors can be taken into consideration as possible causes.

Examination of the properties of the two cements given with the mill analyses in Table 3.1-2 indicate that cement S has a significantly finer grind than cement L, the indicated Blaine fineness values being 3720 and 3275 cm²/g respectively.

The SO₄²⁻ ion concentrations in the paste solutions at early ages, were lower for cement S, and the release of the Na⁺ or K⁺ ion into solution were also lower for cement S. Those indications suggest that cement S has a smaller amount of alkali sulfate immediately soluble to the solution phase than does cement L. As was seen in Chapter 5, SO₄²⁻ in solution interferes with the rapid uptake of naphthalene sulfonate which otherwise takes place.

7.2.2 Effect of Superplasticizers on Inorganic Ion Concentrations in Solution

It is confirmed in all pastes of cement S that gypsum depletion preceded the start of the drop of the sulfate ion concentration in the solution phase. This sequence of two events was clearly observed for the control paste SO, but the overall hydration

was so retarded for the two superplasticized pastes that the progressive decline of the SO_4^{2-} ion in pore solution took place only after 1 day.

The enhancement of the Na^+ ion concentration due to the Na^+ from both superplasticizers, and the subsequent corresponding increases of the OH^- ion concentration at later ages were also seen for both superplasticized pastes of cement S. In the period before set, the alkali ion concentrations were constant regardless of the absorption of the superplasticizers.

The Ca^{2+} ion concentrations were higher in pore solutions for both naphthalene sulfonate and melamine sulfonate superplasticized pastes than for the control mix. This effect was also previously found for the cement L with superplasticizer B. It was confirmed that the amount of gypsum formed immediately from hemihydrate was less in pastes with both superplasticizers. This effect is compatible with the high concentrations of Ca^{2+} produced in the early paste solutions. Generally, it can be interpreted as another symptom of the heavy retardation caused by both superplasticizers. The organics tend to coat the surface of both hemihydrate and cement particles, interfering with the recrystallization of the former to gypsum, and with the hydration of the cements.

For cement S, there seems to be little difference between naphthalene sulfonate superplasticizer B and melamine sulfonate superplasticizer M with respect to their effects on solution phase or calcium sulfate solids composition over time. The plots of the residual concentrations of the naphthalene sulfonate and of melamine sulfonate

over 24 hours were almost quantitatively identical to each other, and the inorganic ion concentration patterns were similar.

7.2.3 Solid Phases

There is a significant difference in the initial CaSO_4 forms of cement S and cement L, in that cement S has both gypsum and hemihydrate while cement L has only hemihydrate. Since hemihydrate converts to gypsum immediately, this difference does not appear to seriously affect the pattern of the CaSO_4 -bearing phase changes. The initial ettringite formation was a little higher with melamine sulfonate than with naphthalene sulfonate, but this did not cause any major change in the rheology of the paste or the absorption of the admixtures from solution.

Again no calcium aluminate monosulfate hydrate was detected at later ages either from the control paste or from the superplasticized pastes of cement S, similarly to cement L. For cement S, the ratio of SO_3 to Al_2O_3 in the mill analysis was 0.70. It is higher than the corresponding ratio for cement L (0.56). Ettringite can be a stable form in a mature paste resulting from this chemical composition, which may be a part of reason for the absence of monosulfate.

From the XRD analysis of the solid samples at 1 day and older, a small broad peak was detected in the d-spacing range of $7.5\text{\AA}$ to $8.2\text{\AA}$. This may be characteristic for several kinds of non- SO_4 -bearing AFm type calcium aluminate hydrated compounds. The peak was significant in some samples. However, it is observed both in the control

pastes and the pastes with the two superplasticizers. Since the control pastes do not show the ettringite peak shoulder on DSC, formation of such phases is not responsible for the shoulder of the ettringite peak.

Between 1 day and 14 days, it appears that the ettringite content in the solid is approximately constant or slightly decreasing for both superplasticized pastes and the control paste of cement S. The apparent decrease may reflect the effect of the complicated figures of the DSC peaks at later ages, rendering the estimates subject to experimental errors. It should be noticed that the total area of the dehydration peaks for hydration products (including C-S-H gel) continues to increase after one day.

7.3 Findings

The following are listed as experimental findings from the experimental work on cement S.

1. Cement S was slower in hydration than Cement L despite its finer grind and higher alkali content. Heavy dosages of both naphthalene sulfonate and melamine sulfonate superplasticizers caused retardation more significantly than for the corresponding pastes of cement L. The degree of retardation founded with this cement hardly differs between the two superplasticizers (at the same dosage) up to 4 days. After that, the paste with melamine sulfonate showed greater hydration than did the paste with naphthalene sulfonate.
2. The time dependent patterns of the concentration of admixture remaining in solu-

tion were practically identical for both the naphthalene sulfonate and melamine sulfonate superplasticizers.

3. The analytical calculation to associate polymer anion concentrations with excess cation over anion charges of the inorganic species, developed in the previous chapter, was applied for the superplasticized pastes of cement S. It appeared to yield appropriate results, at least for the first day, when the amount of superplasticizer remaining in solution was large enough to be accurately measured. It was found that the calculated charge density of the residual dissolved patterns of both admixtures were not constant and increased as absorption of the superplasticizer proceeded, especially for melamine sulfonate.
4. The effects of the two superplasticizers on the solution phase ion concentrations were similar. Compared to the control paste SO, both produced Na^+ ion enhancement derived directly from the superplasticizers, and subsequent corresponding OH^- ion enhancement at later ages; enhancement of the Ca^{2+} ion concentration in the period before setting; and enhancement of the concentration of SO_4^{2-} during the early plateau period.
5. Although the form of CaSO_4 in cement S was a mixture of gypsum and hemihydrate, and thus different from the entirely hemihydrate form in cement L, the results of the time-dependent solid phases analyses were similar for both cements; the hemihydrate in cement L had entirely converted to gypsum within one hour.
6. No calcium aluminate monosulfate hydrate was found in any solid sample for

cement S.

7. The quantitative analysis of ettringite by DSC in older paste was found difficult again for the cement S, because of several effects. Non-sulfate-bearing AFm compounds, detected by x-ray diffraction, may be contributing to the ettringite DSC peak at later ages. Another feature at later ages is the progressively developed broad C-S-H peak from which the ettringite peak must be separated. Further, it was found that the characteristic dehydration peak of ettringite in many pastes exhibited a significant shoulder in a higher temperature side when either superplasticizer was present, which is probably attributable to incorporation of these admixtures into the ettringite phase. Consequently, the ettringite content determined by DSC becomes more variable at later ages.

CHAPTER EIGHT

DISCUSSION AND IMPLICATIONS

8.1 Factors Affecting the Removal of Superplasticizer from Solution

8.1.1 General

The removal pattern of the superplasticizers from solution was similarly observed in all the superplasticized pastes. A large portion of the superplasticizer in the mix water is absorbed to the solids by the first measurement (usually about 15 minutes). Then the concentration of the remaining superplasticizer stays nearly constant or decreases very slowly for several hours depending on cement system. Subsequently, a rapid decline of the residual concentration of superplasticizer occurs at usually sometime between 12 and 24 hours, and only a small amount remains indefinitely thereafter.

The amount of the initially removed superplasticizer varies with the cement system, and probably with the inorganic ions present in the paste solution. In some cases with white cement W, almost all the superplasticizer was removed from the solution immediately. The pastes usually showed a rapid premature stiffening for these cases. The white cement has a peculiar chemical composition; it has a very low alkali con-

tent, a low aluminate content, a very low iron content, and the CaSO_4 contained is entirely "insoluble anhydrite". The immediate absorption of essentially all of the superplasticizer and the subsequent rapid stiffening of the pastes are considered to be an example of incompatibility problems between cements and admixtures.

Especially, it was observed in this particular white cement that the initial absorption of the superplasticizer could be changed by changing the mixing procedure, even for pastes of nominally identical compositions. No such effect was found for the other two cements, both of which were more nearly "normal" gray portland cement.

Not only can variation in the original mix procedure affect the superplasticizer response, but it was also found that remixing can cause additional removal or release of the superplasticizer by the solids with this sensitive white cement. It should be noted that the interaction between superplasticizer and hydrating solids are not simple, and are sensitive to slight changes of various factors. The white cement appears particularly sensitive to such effects.

The absorption of naphthalene sulfonate also varied considerably with addition of sulfate which will be discussed in detail later. The more nearly pure naphthalene sulfonate was absorbed by the white cement nearly completely with a few minutes; if sulfate ion in appreciable concentration was present, the immediate absorption was much reduced, with drastic consequences for the rheology of the paste.

The melamine sulfonate, which had some sulfate impurity content, underwent a considerable amount of initial absorption by the white cement, but left a substantial

residual concentration. This initial response resulted in phenomena quite different from what was produced either by the nearly pure naphthalene sulfonate or by the impure, sulfate-rich naphthalene sulfonate, specifically a complete retardation for two days.

In comparing the response of the melamine sulfonate with naphthalene sulfonate on the ordinary gray portland cements, no such drastic differences in behavior were found. For example, with cement S, equal dosages of both superplasticizers produced rapidly equal initial absorptions, and similar patterns of removal with time were found thereafter. The rheological effects, and the time dependency of their effects were quite similar.

8.1.2 Relation Between Ettringite Formation at Very Early Ages and Superplasticizer Absorption

Fig. 8.1-1 shows that the amount of superplasticizer removed from solution by the first measurement (usually about 15 minutes) expressed as the weight ratio normalized to the original cement weight, and the ettringite formed during the same period for the various mixes carried out in this study.

In the figure, it is clearly seen that the amounts of the ettringite formed (by the first measurement at about 15 minutes) are linearly correlated with the amounts of the superplasticizer removed from solution in the same period. The data include results for three different cements with two different superplasticizers; even so, the fit of the

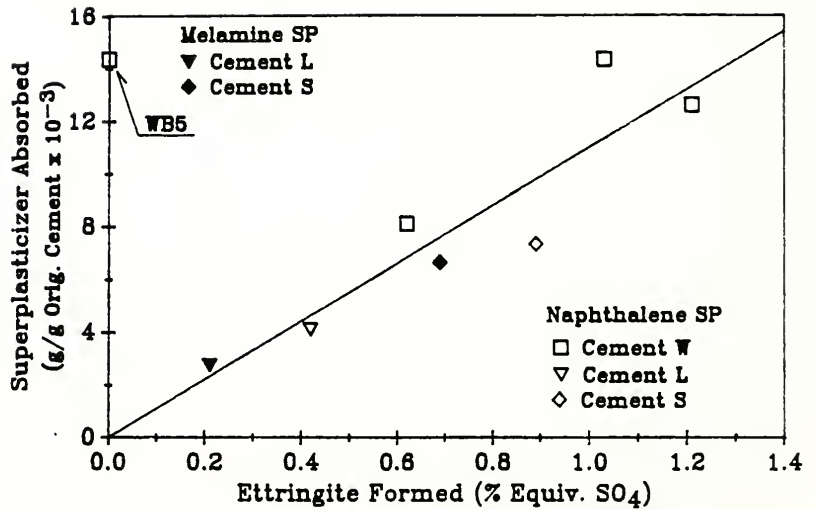


Fig. 8.1-1 The amount of superplasticizer removed from solution within the first 15 minutes of hydration vs. ettringite formed during the same period

regression line is quite good ($R = 0.908$). This correlation between superplasticizer removed from solution and ettringite formed at the same time is taken as strong evidence that the removal process is primarily that of incorporation of superplasticizer into or with newly forming ettringite.

The regression line drawn in the figure is for all data secured in this research except one point. This single outlier point is for the paste of white cement with 1.2% Na_2O equivalent of KOH added in the mix water (WB5). This paste exhibited rapid set and almost complete removal of the superplasticizer from solution, but no ettringite was observed for the first 2 hours of hydration. As discussed in Chapter 5, these phenomena were related to rapid $\text{Ca}(\text{OH})_2$ precipitation that was associated with the very high initial concentration of the OH^- ion in the paste solution. The removal of the admixture was considered to have occurred under very different conditions from all of the other cases.

8.1.3 Sulfate Ion Effects in Paste Solutions

Experimental work on white cement W in Chapter 5 appeared to indicate that the higher the SO_4^{2-} ion concentrations in the mix water, the less the initial uptake of the naphthalene sulfonate superplasticizer from solution. For the two gray cements L and S, both of which showed higher early SO_4^{2-} ion concentrations, the initial removals of both superplasticizers from solution were much less than those for the white cement.

The removal of the admixture from solution can be affected by many factors other than the early sulfate ion concentration. The content of C_3A and C_4AF , and the fineness of the grind may both be significant in this respect. The two cements L and S both have much larger contents of the aluminate phases than the white cement dose. Despite this, the results were opposite to what may have been expected on this basis. While no data on the fineness of the white cement was provided, it gave indications of being considerably finer than the two gray cements. This presumed higher surface area might have contributed somewhat to the higher absorption.

Nevertheless, the main reason for the smaller initial absorption with the gray cements is considered to be the higher sulfate ion concentrations in solution. The alkalis in the clinker of both cement L and S mostly exist as alkali sulfates or alkali calcium sulfates, and they dissolve to the mix water quickly and release SO_4^{2-} ions immediately. Also, the hemihydrate in these cements was found to dissolve fairly rapidly, also releasing a considerable amount of sulfate. Thus the sulfate ion concentration at the first measurement for the control pastes without superplasticizer for both gray cements were much higher than that for the white cement. This high initial SO_4^{2-} ion concentration can be considered equivalent to the adding of the SO_4^{2-} in the mix water for the previous experiments for the white cement.

It appears that in superplasticized systems, when a high concentration of SO_4^{2-} ions is present in the early solution phase, the production of early, perhaps poorly crystalline, ettringite is reduced, and less of the superplasticizer is absorbed by the hydrating solids. In some cases also, the superplasticizer molecules taken up early by

the poorly crystalline ettringite are not necessarily permanently removed from solution. It is found for the white cement that an appreciable portion of this "absorbed" naphthalene sulfonate can be released back to the solution initiated by various causes, such as an addition of sulfate.

8.1.4 Hydroxide Ion Effects in Paste Solutions

Some pastes of the white cement were made with KOH dissolved in the mix water along with the naphthalene sulfonate superplasticizer. It is rare in real cement systems that the mix water is conditioned with alkali hydroxides. Some peculiar phenomena were observed in the superplasticized paste with large KOH additions (1.2% Na_2O equivalent). First, the calcium sulfate anhydrite phase was dissolved very quickly and released considerable amounts of both Ca^{2+} and SO_4^{2-} ions to the solution phase. Second, a vigorous precipitation of $\text{Ca}(\text{OH})_2$ was observed and attributed to the limited amount of $\text{Ca}(\text{OH})_2$ that can remain in solution in slightly alkaline systems due to the common ion effect, coupled with the large amount of Ca^{2+} dissolved from CaSO_4 . Third, gypsum was not precipitated, and even ettringite was not observed for the first 2 hours. It is thought that these effects are not due to the special properties of the white cement or of the superplasticizer, but may be more general effects of a very high OH^- ion concentration in the solution phase.

8.1.5 Effects of the Form of Calcium Sulfate in the Cement

The three cements examined here contain calcium sulfate in forms different from each other. Cement L has only hemihydrate, and cement S contains both hemihydrate and gypsum. The white cement W contains only insoluble anhydrite as the initial form.

Comparing the two control pastes of the gray cements L and S, it was found that this difference in initial form of calcium sulfate did not significantly affect the hydration behavior as monitored by the analyses of solution phases and of the solid phases. The hemihydrate dissolved immediately after the initial contact with water, and converted to gypsum almost instantaneously. Thus the calcium sulfate observed to be present after 15 minutes was entirely gypsum for both of these control pastes.

When superplasticizer was introduced to the systems, a delay of this conversion from hemihydrate to gypsum was observed. In some superplasticized pastes, hemihydrate was found to be still present between 15 minutes and 1 hour. It is considered that the superplasticizer was either adsorbed on or incorporated with the surface of the hemihydrate particle, and hindered its dissolution. This is the only difference found to originate from the difference between hemihydrate and gypsum as the initial form in the unhydrated cements, and its effect is considered to be small.

In contrast, the hydration behavior of the superplasticized pastes of white cement W were found to be very different from those for other ordinary portland cements L and S. Although other chemical and physical parameters of the white cement were

different from those for cement L or S, some of the characteristic effects observed can be specifically attributed to the insoluble anhydrite form of the gypsum.

It is possible that insoluble anhydrite absorbs some of the superplasticizer, and that the dissolution of anhydrite is thus delayed, similarly to the effect of superplasticizer on hemihydrate as seen previously. However, no such hindrance of dissolution was observed by the first measurement in any superplasticized paste of the white cement. Rather, the initial dissolution of insoluble anhydrite was somewhat promoted, compared to that found for the control paste, i.e. the reduction in the anhydrite content within the first 15 minutes was greater with superplasticizer. The reason is not clear. It may possibly be explained as an effect of greater wetting of the anhydrite due to the well dispersed state of the cement particles indicated by the action of the superplasticizer.

The rapid stiffening exhibited in some superplasticized white cement pastes did not occur for the superplasticized pastes with additional alkali sulfate in the mix water (WBN, WBK). The lack of the SO_4^{2-} ion in the solution phase at very early ages is considered to be the primary cause for the rapid stiffening; almost all of the superplasticizer was immediately removed by the cement under these circumstances. The low SO_4^{2-} ion concentration was a function in part of the very low content of alkali sulfate in this cement. It was further seen to be associated into the fact that only anhydrite, which has the slowest rate of dissolution of the CaSO_4 forms, was present. Even the alkali content in an original cement was low, the SO_4^{2-} ion concentration would become reasonably high if the CaSO_4 in the cement were hemihydrate or gypsum

forms.

8.2 Effects of Superplasticizer on Properties of Paste

8.2.1 Effects of Superplasticizer on Physical Characteristics of Pastes

It was found that the physical characteristics of pastes are associated with the superplasticizer concentration remaining in the solution phase. The fluidity of the paste (represented by the spread in area of the mini-slump cone test) was particularly closely related to the concentration of the superplasticizer remaining in the solution. When the residual concentration of the superplasticizer became so low that the residual superplasticizer was primarily monomer, the paste exhibited stiffening. There was no exception to this generalization.

Generally, the superplasticizer adsorbed on the surface of the particles is considered to provide a negative surface electric charge, leading to repulsion of particles of the same charges suspended in solution and effective dispersion. During cement hydration, the electric charges on the solid surface become ineffective by being covered with newly formed hydration products. Residual superplasticizer in solution is able to adsorb again to the new surface, and to maintain the dispersive state. Hence, an excess amount of superplasticizer in solution is considered to be necessary to maintain the fluidized state of the paste. In these pastes, the residual concentration of the superplasticizer was found to be generally an indicator of existing degree of fluidization of the paste.

8.2.2 Effect of Superplasticizer on Retardation in Hydration

All three superplasticizers A, B, and M exhibited a retarding effect. Since the dosage of the superplasticizers was high, the hydration of the well-fluidized pastes were considerably retarded. Even the superplasticized pastes of white cement W (WB0) that showed a stiffening at very early ages, showed delays in both the time of the second peak of heat evolution and in the time of set, as compared to the control pastes. However, the delay of the set time caused by the superplasticizer was shorter for the white cement than for the two gray cements.

The retardation effect may possibly be associated with an alteration of the hydration products formed, especially the ettringite. Ettringite formed in the presence of superplasticizer in solution appears to have absorbed significant contents of the superplasticizer molecule. This may modify the early ettringite and render it a more efficient barrier to further hydration of the unhydrated portion of the cement particles.

The two superplasticized pastes of the white cement batched with additional alkali sulfates in the mix water (WBN, WBK) exhibited considerable retardation, and otherwise behaved more normally like the superplasticized gray cements. Thus, even though the calcium sulfate was insoluble anhydrite, the cement behaved normally when a sufficient amount sulfate ion was made available in solution at very early stages of hydration. Without the added sulfate ion, the superplasticized white cement pastes behaved abnormally.

8.2.3 Effects of Superplasticizer on Solid Phase and on the Solution Phase

The analyses of CaSO_4 bearing compounds indicated that the time-dependent change of these compounds are basically the similar for the two ordinary portland cements. The hemihydrate in the unhydrated cements is converted to gypsum immediately at the beginning of hydration. The content of this "secondary" gypsum is gradually reduced toward zero, in the same way that "primary" gypsum is reduced when it is the only CaSO_4 constituent. After the gypsum is used up, the SO_4^{2-} ion concentration in paste solution starts to decline. Ettringite forms rapidly at very early ages, then continues to form at a slower rate.

For the white cement, the patterns are different from those for the other cements. The insoluble anhydrite content gradually diminishes as hydration proceeds, but the anhydrite does not convert to gypsum. The pattern of the ettringite formation is actually quite similar to that experienced with gray cements.

With introduction of either superplasticizer to the cement systems, some changes are observed in the solids. For the gray cement with hemihydrate, the amount of the gypsum formed in early stages is reduced compared to the paste without superplasticizer. For both gray cements, the gypsum stays longer than in the control pastes. For all three cements, the formation of ettringite after the end of the initial sudden ettringite production period is considerably slower with superplasticizers. Consequently, the period of constant ettringite content was much longer and was observed more prominently with superplasticizer. These outcomes are considered to be another retardation

effect due to the superplasticizer.

The important effects of the superplasticizer on the solution phases were the enhancement of the Na^+ ion concentration, and the subsequent corresponding increases in the OH^- ion concentration at later ages. These phenomena were observed for all three cements.

8.3 Analyses of CaSO_4 -Bearing Phases

The methodology applied in this study for quantitatively tracking SO_4 in solids by using DSC, was shown to be practical. Its possibilities and limitations have been clarified. It is an strong advantage that ettringite, hemihydrate, and gypsum can be quantified simultaneously by a single run of the DSC, without complicated pre-treatment.

Even with the relatively facile experimental procedure, the contents of those three compounds as determined by the area of dehydration peaks, are fairly accurate. Those of the calcium sulfate hemihydrate and the gypsum are particularly accurate, since the characteristic dehydration peaks for these solid phases are reasonably distinct. However, discussed in Chapter 6 and Chapter 7, the determination of ettringite is complicated by increasing development of the C-S-H gel, the possible production of C_4AH_x -type compounds, and the incorporation of the superplasticizers, especially at older ages than 1 day. The ettringite measured here is probably much less crystalline than other calcium sulfates; thus the characteristic dehydration peak is observed at

lower temperatures.

The determination by DSC is considered to be more accurate than by methods such as QXRD. However, the anhydrite phase present must be determined by QXRD analysis, since no thermal analysis method can be used. This quantitative analysis is subject to larger deviations than those found in DSC analysis.

However, it must be recognized that the combination of the DSC analyses developed here and the x-ray diffraction analysis for insoluble anhydrite is still incomplete, even for the original unhydrated cement. The sum of the SO_4 contents of all the solid phases was less than the cement sulfate content reported in the mill analysis for all three cements. Alkali sulfates and alkali calcium sulfates were not accounted for, and the possibly presence of some soluble anhydrite along with the hemihydrate in cements L and S could not be taken into account. The systems after water was added, were also incompletely evaluated with respect to sulfate. It is well known that at later ages sulfate ions are captured by C-S-H gel. This sulfate cannot be quantified easily either.

In addition to those sulfates not accounted for, different quantitative analysis methods have different degrees of variations in results, so that the combined balances are not so accurate. However, it does appear that time-dependent changes of each CaSO_4 -bearing phase determined by the DSC analysis is correctly monitored, even though the sum of all of the sulfate present cannot be completely apportioned.

CHAPTER NINE

FINDINGS AND CONCLUSIONS

9.1 List of Findings

The following is a list of detailed findings resulting from the experimental work carried out in this study.

1. At the high dose levels used, both naphthalene sulfonate and melamine sulfonate superplasticizers had a retarding effect on the hydration of all the cements examined. The retarding effect was observed in calorimetry, in measurement of non-evaporable water content with time, in measurements of the disappearance of gypsum and the appearance of ettringite with time, and in measurements of the pattern of changes in the solution phase diminishing with time.
2. The superplasticizers used also produced retardation in setting time for all three cements, except for certain cases with the white cement, in which premature setting occurred.
3. The white cement examined here is described as very low alkali content, low aluminate phase content with almost no iron content, and with insoluble anhydrite being the only form of calcium sulfate present. Due to this peculiar composition, this white cement was found to be very sensitive in interaction with the

superplasticizers. In addition to other admixture interaction effects, it was found that the degree of absorption of the superplasticizer by the hydrating cement can be even changed by changing the mixing procedure. This kind of sensitiveness is not observed for either of two ordinary gray portland cements used.

4. Pastes of this white cement mixed only with a relatively pure naphthalene sulfonate superplasticizer exhibited rapid stiffening rather than the expected dispersing effect. This is considered to be an incompatibility problem between the cement and the admixture. This stiffening is associated with formation of a large amount of ettringite at very early ages, coupled with an almost complete removal of the superplasticizer from solution.
5. Two different naphthalene sulfonate superplasticizers produced significantly different early behavior with the white cement. Pastes mixed with a less pure naphthalene sulfonate superplasticizer containing sodium sulfate impurity, did not undergo premature stiffening, but exhibited the expected dispersing effect. This normal behavior was reproduced using the pure naphthalene sulfonate superplasticizer when dosage of Na_2SO_4 "impurity" identical to that present in the less pure superplasticizer was added to it.
6. It was found that addition of the sulfate ions into the mix water reduces the initial removal of naphthalene sulfonate by the white cement. The presence of a reasonable concentration of sulfate ion in the mix solution results in maintaining a reasonably high residual concentration of naphthalene sulfonate in solution. This

appears to be necessary to prevent the premature stiffening. By itself, the insoluble anhydrite present in the white cement does not dissolve rapidly enough to maintain the needed sulfate in concentration.

7. While the removal of naphthalene sulfonate from solution by the hydrating white cement is affected by sulfate ion addition, similar dosages of K_2SO_4 and Na_2SO_4 exhibited only slight differences in the absorption patterns.
8. It is found that addition of OH^- ions to the mix water also affected the absorption of naphthalene sulfonate from the mix solution of the superplasticized white cement paste. With the less pure superplasticizer, the initial uptake increased with increase in the initial OH^- ion concentration of the mix water. However, the reaction pattern of the pastes altered differently with different dosages of KOH, and the differing uptakes of superplasticizer cannot be explained by one comprehensive mechanism.
9. It was found specifically that an 0.6% KOH addition to superplasticized white cement paste with either naphthalene sulfonate superplasticizer produced a peculiar response, such that most of the superplasticizer initially removed from solution by the solid phases, was subsequently released back into solution, and then absorbed again. This response was entirely reproducible. Similar, but weaker responses of the same kind were observed with slightly greater and with slightly smaller additions of KOH.
10. As the dosage of KOH was increased, the rate of dissolution of insoluble anhydrite

in the superplasticized pastes of the white cement was accelerated.

11. With a very high dosage (1.2%) of KOH, the white cement paste with the pure naphthalene sulfonate exhibited an unusual kind of quick setting behavior. Instead of the expected retardation effect with superplasticized pastes, this paste stiffened in about 10 minutes and set in about 5 hours. A large amount of Ca(OH)_2 was precipitated quickly, and ettringite did not form for the first 2 hours. These phenomena are related to the high initial pH of the mix solution.
12. No hydrated form of calcium sulfate was found at any time in any of the hydrated pastes of the white cement. This was true regardless of the presence of naphthalene sulfonate superplasticizer or of added amounts of SO_4^{2-} or OH^- ions. For the pastes of moderately alkaline solution (i.e. with little or no added KOH), the slow rate of dissolution of anhydrite appears to restrict the sulfate ion concentration to values less than the saturation level of calcium sulfate (80 meq/L). For the pastes of higher initial OH^- ion concentration, i.e. those with substantial amounts of added KOH, gypsum did not precipitate despite the increased level of sulfate in solution.
13. A heavy dosage (2% by weight of cement) of a melamine sulfonate superplasticizer severely retarded the setting of the white cement. The paste remained fluid and completely dispersed, with bleeding evident, for almost two days. The residual concentration of the admixture in the paste solution remained quite high during the corresponding two day period.

14. The time dependent patterns of the concentration of admixture remaining in solution were studied for some of the materials examined. In studies with one of the ordinary portland cements used, it was found that these time-dependent absorption patterns were practically identical for both the naphthalene sulfonate and melamine sulfonate superplasticizers, dosed at the same weight concentration.
15. The sulfate ion concentration in paste solution at its "plateau" level (before the sudden drop) was higher in the presence of superplasticizers. This was a transient effect, since the existence of the constant SO_4^{2-} ion plateau is limited in time, and eventually the SO_4^{2-} ion concentration decreases to negligible amounts.
16. It is found that the Ca^{2+} ion concentration in the pore solution of the superplasticized pastes is higher than that observed for the corresponding pastes without superplasticizer. This was true while the paste was well dispersed, and while the residual concentration of the superplasticizer was reasonably high. At older ages (usually after 1 day), the Ca^{2+} ion concentration drops to near zero with the superplasticizer, as it does at an earlier age without the superplasticizer.
17. Both superplasticizers are thought to be made up of polymers of varying chain length. It is known that the less pure naphthalene sulfonate superplasticizer contains a significant content of monomer molecules, i.e. "polymer" of single molecular units, and that these are not absorbed by cements. The proportion of monomeric naphthalene sulfonate remaining in the paste solution as a function of time was studied by analyzing two characteristic peaks in the UV absorption spec-

trum. It was confirmed that when the dormant period had ended and the cement had started its rapid hydration phase marked by the second hydration peak, nearly all of the polymeric chain molecules were taken up by the hydrating cement, leaving mostly monomeric molecules in solution.

18. All of the cement pastes studied, regardless of the presence or absence of superplasticizer, produced ettringite as the only sulfate-bearing crystalline hydration product. No calcium aluminate monosulfate hydrate was detected in any sample of any of the three cements. This was true for hydrating pastes of the two ordinary portland cements studied up to 14 days, and was true even though the sulfate concentration in the pore solution was virtually zero after 3 day. This absence of detectable monosulfate was not expected.
19. At older ages (3 days and beyond), a small broad x-ray diffraction peak was sometime detected at the d-spacing of about $7.9\text{\AA}$ in pastes of both ordinary portland cements studied. This was attributed to the formation of non-sulfate-bearing AFm compounds. It was observed in pastes both with and without superplasticizers.
20. A method was developed for studying the rates of dissolution of insoluble anhydrite, the conversion of hemihydrate to gypsum, and the rate of decomposition of the gypsum in the reacting cement pastes. This was applied throughout this study to secure information concerning the effects of the admixtures on these processes. The method was repeated DSC analysis of solids filtered from the cement pastes as a function of time.

21. The same method of DSC analysis was found to be suitable for the quantitative evaluation of the amount of ettringite being produced in the same pastes. However, several problems were associated with ettringite analysis by this method for older pastes.
22. It was found that the characteristic DSC dehydration peaks of both ettringite and gypsum in some pastes exhibited a significant shoulder on the higher temperature side when either superplasticizer was present, and not when superplasticizer was absent. These peak shoulders are thought to be due to absorption of admixtures by, or into the ettringite or gypsum, respectively.
23. It was found useful to express the total of the solid CaSO_4 -bearing phases detected (including ettringite) and the sulfate ions in solution re-expressed in terms of equivalent sulfate content, as a function of time. The total sulfate quantified in this method was less than the total cement sulfate analysis because alkali or other clinker borne sulfates were not accounted for in the early stages, and sulfate incorporated in C-S-H gel was not accounted for in the late stages. Nevertheless, various interactions with the superplasticizers were pinpointed by changes produced in the sulfate systems as measured by this tally.

A number of findings related specifically to the analytical methods used or to their application can be summarized below.

- a. The measurement of melamine sulfonate by UV analysis is interfered by the OH^- ion in the solution. This interference is found to be effectively eliminated by

neutralizing with sulfuric acid prior to the UV analysis.

- b. It was confirmed in preliminary study that pure gypsum is dehydrated to soluble anhydrite by heating to 160°C, and that this soluble anhydrite is rehydrated instantaneously to hemihydrate under the normal humidity conditions at room temperature.
- c. Synthesized calcium sulfoaluminate monosulfate hydrates showed several complicated dehydration peaks on DSC. However, the major peak always appeared in the temperature range between 200°C and 300°C. The complete absence of monosulfate in the experimental pastes reported in this work is confirmed by that fact that no peak was observed in this 200°C - 300°C temperature range with any of the samples studied.
- d. A synthesized C_4AH_{13} sample (with some carbonation) also analyzed by DSC, showed a strong response between 230°C and 300°C, which is considered to be characteristic of this calcium aluminate hydrate compound when well crystallized.

9.2 Conclusions

The conclusions established as a result of the study are as follows:

1. A new approach to the study of the interactions between superplasticizers and cements has been developed in this research. The new features include time-dependent analysis of the calcium sulfate-bearing phases by DSC and by x-ray diffraction, coupled with similar time-dependent analyses of both superplasticizer

and inorganic ions in the paste solutions. This approach was found to be very effective in studying the nature of superplasticizer effects, and the same methods can be adopted to the study of the interaction effects that may be produced by other kinds of chemical admixture.

2. A key element in this approach is DSC analysis of changes in the contents of gypsum and hemihydrate as the pastes react with water. The same DSC runs are also used to study the rate of formation of ettringite. The rate dissolution of insoluble anhydrite (where present in a given cement) cannot be studied by DSC, but requires quantitative x-ray diffraction analysis. The content of soluble anhydrite is not determinable, but experiments indicate that soluble anhydrite is not stable in laboratory air and converts immediately to hemihydrate. The quantitative analysis of ettringite for later age is complicated by increasing development of the C-S-H gel, the possible production of C_4AH_x -type compounds, and incorporation of the superplasticizer on or within ettringite.
3. The rheological effectiveness of superplasticizer appears to depend on maintaining a reasonable concentration of molecules of the proper chain length in solution. The tendency appears for the hydrating cement to preferentially absorb the effective polymeric molecules and leave a greater proportion of ineffective monomer molecules in solution as hydration proceeds.
4. The rheological effectiveness of naphthalene sulfonate superplasticizer also is associated with the content of sulfate ions in solution. Cement pastes lacking a

reasonable concentration of sulfate ions do not show the expected dispersive effect of the superplasticizer, and stiffen and set prematurely. This response is associated with rapid removal of nearly all the superplasticizer from solution by the hydrating cement, coupled with simultaneous formation of a very large amount of ettringite. When soluble sulfate is supplied to such cement systems, the early uptake of superplasticizer is reduced, the rate of ettringite formation is decreased, and the admixture produces its normal dispersing action on the cement.

5. In "normal" superplasticized cement pastes, the time pattern of ettringite development is different from that of corresponding admixture-free pastes. With the superplasticizer present, ettringite production during the first few minutes of hydration is very rapid. The content of ettringite then remains constant for some hours before again starting to increase. This behavior is very different from what is found in similar pastes without superplasticizer, in which ettringite production does not stop, but is continuous through at least the first day of hydration. This difference is considered to be in part an expression of the retardation effect produced by the superplasticizer.
6. The presence of superplasticizer strongly affects the nature of development of the sulfate-bearing compounds in the early stages of cement hydration. When the total of the crystalline sulfate-bearing compounds (gypsum, hemihydrate, insoluble anhydrite, and ettringite) is added to the total sulfate found in solution at each stage of the early reaction processes, it is found that the total amount detected is much reduced in the presence of the superplasticizer. This reduction is attributed

mostly to poor crystallinity of the solid products in which the superplasticizer is absorbed or incorporated.

7. Both naphthalene sulfonate and melamine sulfonate superplasticizer used in this study were primarily Na^+ neutralized, as are most commercial superplasticizers. Use of such superplasticizers results an immediate increase in the Na^+ ion concentration of the pore solution, as the superplasticizer is dissolved and the balancing cation of the sulfonate groups is ionized. Subsequently, as the polymer is absorbed from the solution by the hydrating cement solids and its sulfonate groups correspondingly removed from the solution, they are replaced by OH^- ions, leading to a permanent increase in the OH^- ion concentration of the paste solution. This may produce a greater tendency to alkali aggregate reaction damage if susceptible aggregates are used.
8. In pore solutions of pastes incorporating superplasticizers, it was found that the sum of inorganic cations consistently exceeded the sum of inorganic anions. It was established that this apparent lack of charge balance was due to neglect of the anionic sites (exposed sulfonate groups) on the polymeric chains of the dissolved superplasticizers. As the superplasticizers were removed from solution by the hydrating cements, this apparent discrepancy was reduced.
9. An measurement of the apparent charge density (meq/g) of the overall superplasticizer was developed, involving paired measurement of the apparent discrepancy between positive and negative inorganic ions and weight concentration of dis-

solved polymer. This produced fairly consistent estimates of charge density of residual polymer in solution for naphthalene sulfonate (about 4.8 meq/g) and similar, but more variable estimates for melamine sulfonates. However, in the later stages when absorption of superplasticizer was more nearly complete, the calculations broke down because of inaccuracy in measurement of the content of the small amount of residual polymer remaining in solution.

10. It was found that conversion of hemihydrate to gypsum was completed by 15 minutes in the absence of superplasticizers, but that completion of this normally rapid process was appreciably delayed in the presence of superplasticizers. Subsequent to this conversion, no distinction was found between rates of dissolution of primary gypsum and secondary gypsum produced from hemihydrate.
11. In all cases examined with and without superplasticizer, the decline in sulfate ion concentration in the paste solution was preceded by the exhaustion of the solid gypsum.

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